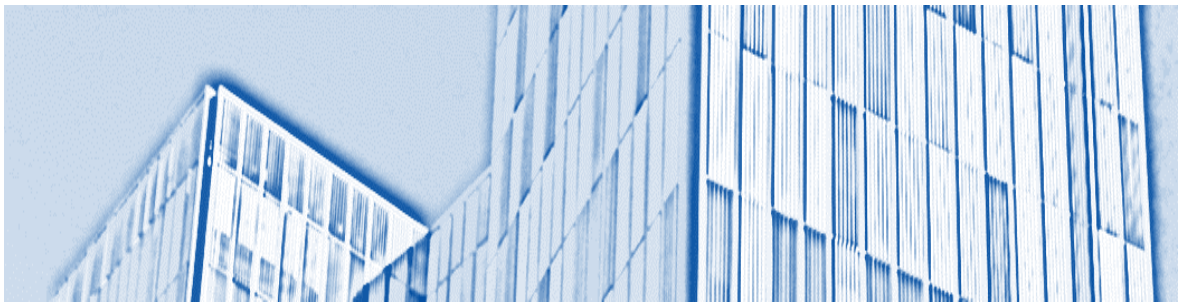
UNIVERSITAT POLITÈCNICA DE CATALUNYA
BARCELONATECH
Escola d'Enginyeria de Barcelona Est

MASTER THESIS REPORT

Materials science and engineering

DEVELOPMENT OF NEW MATERIALS FOR HYDROGEN STORAGE



Memory

Author: Killian Durand
Director: Jose Antonio Benito

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Abstract

Hydrogen could be one the most efficient source of energy in the future.
The problem which is remaining about this energy is storage. Indeed, it is still very hard to store hydrogen due to the volume that it takes in its liquid and gaseous.
The solution could be solid storage of hydrogen using metal hybrids which are able to absorb it. By storing hydrogen with this method, the gains of volume and safety are very high.
One of the metals which could be used is Magnesium, but it is necessary to create alloys in order to have even better properties. In this project, different magnesium alloys have been tested (Mg, MgTi and MgTiFe). These materials, in powder form, were milled for different times thanks to a planetary milling process in order to improve some of their properties (mainly remove oxide layer, specific surface area, particle size distribution). After that, these materials were tested on a system created by the PROCOMAME group in order to obtain results about hydrogen absorption.
The morphology, the particle size distribution and the specific surface area of the milled powders were characterized by different techniques. In addition, X-ray diffraction patterns were obtained to check if mixing in solid solution was achieved during milling. There is a very large increase of the specific surface of powders, although the average particle size remains nearly the same due to the agglomeration of the small milled particles. On the other hand, neither a solid solution or intermetallics were found which means more milling time is required to get the total mixing.
Regarding hydrogen absorption tests, indeed milling these materials help to destroy the oxide layer which unable the hydrogen absorbance. The absorption percentages are significant but not very large, and it was found that the hydrogen absorption of the powders seems to be related to the specific surface area and the particle size distribution and that there is no effect of Ti and Fe additions to Mg in the absorption starting temperature, at least in the tested milling conditions.

Acknowledgments

6 months after the beginning of this work, I end my internship at the PROCOMAME as a master student of EEIGM.

I wanted to thank all the people I met during this internship which brought me a lot and helped me to become more efficient, more autonomous but also more rigorous.

To my mother, who always supported me in my studies, encouraged me in the worst as in the best moments and taught me to never give up. To my sisters who brought me a lot of courage during my whole studies. To Mathilde, who gave me love and support since day one in my materials engineering studies.

To Brian and Cyril for their happiness and their jokes in our apartment.

To Toni Benito, for his patience, his kindness and his guidance in my first experience in the scientific research even if it has been difficult to manage all the problems.

To Casimir and Kim who taught me a lot about the work inside the laboratory and spent hours to help me managing the problems.

To everyone I may forget,

Thank you.

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1. Introduction – State of the art

1.1. H2 as a new source of energy

Every day, a lot of energy is consumed, especially energy from fossil fuels. Unfortunately, it has terrible consequences on environment and create irreversible damages to the planet. In order to avoid this, the solution is clean and renewable energy. The demand of these energies has increased a lot during last years. To manage this demand, hydrogen could be used as a source of energy. It has become one of the most important point to work on to manage the future of energy. [1][2]

This source could be very efficient for different reasons. Indeed, Hydrogen is the most abundant element on earth with 74% of weight molar abundance in universe but this is also the lightest element of the universe. Furthermore, hydrogen is also a clean source of energy. To produce energy with hydrogen, there are no chemical consequences and the only by-product of the use of hydrogen as a source of energy is water. Then, there are no greenhouse gases or pollutants emitted.

All these advantages make hydrogen really interesting, but it is necessary to also consider all the drawbacks. First, the production price is very high. Moreover, it is hard to store hydrogen and that is why it is necessary to find a material able to store it without too many drawbacks.

1.2. The storage of hydrogen

In order to be efficient while storing hydrogen, the goal is to use less energy as possible but also less materials as possible. Indeed, the most important thing to store hydrogen is the choice of the material. The main problem is the volume that takes hydrogen. Nevertheless, the volume which is used by hydrogen depends on its state. Currently, progress is still needed in order to make hydrogen a viable source of energy. It is necessary to find a way to store hydrogen with a high density in order to save space. The known methods to store hydrogen concern liquid and gas hydrogen but it requires a lot of volume.[3] That is why, solid state hydrogen storage could be the solution despite the different obstacles as the high flammability which is really dangerous and has to be treated with precautions.

1.2.1. Storage of compressed hydrogen

This method of hydrogen storage is the most common because it is the easiest one and the simplest one. Indeed, it is just necessary to compress hydrogen at a really high pressure in

order to reduce the volume taken by it. Compressing hydrogen reduce the volume needed by 99,6%. Indeed, without compressing hydrogen, the volume needed to store 1kg of hydrogen would be 12.3 m3 while with compressing the required volume to store 5 kg of hydrogen would be only 212 liters. [4]The range of pressure used most of the time is quite high, between 350 and 700 bars. Without this pressure, it is useless to use this method because the quantity of hydrogen stored would be too small to be used for many applications as vehicle for example. Nevertheless, it is important to notice that this method has a small volumetric energy density and also a really high cost due to the materials used to contains very pressurized hydrogen. Furthermore, it is important to manage safety issues in order to avoid any kind of explosion due to the high pressure.

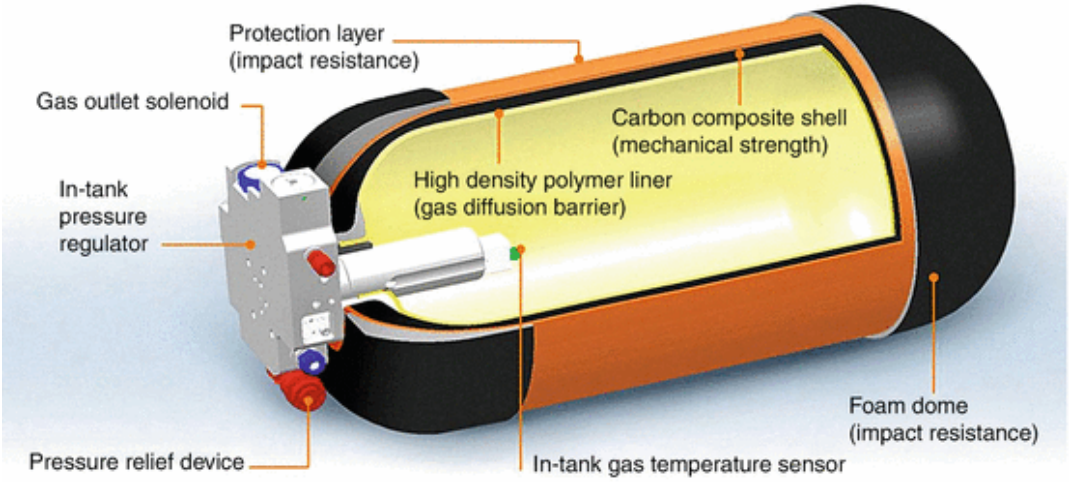

Figure 1 : Compressed hydrogen tank [5]

1.2.2. Storage of liquified hydrogen

It is also possible to liquify hydrogen by reducing its temperature to 20,4K at an atmospheric pressure. Nevertheless, to use this method, it is necessary to have a very efficient heat insulation with a high adiabatic efficiency. Indeed, if the hydrogen is stored in a non-insulated tank, its vaporisation will occur at a latent heat of 7.56 kCal per litre.

Heat transfer could be divided in three parts which are radiation, conduction and convection. In order to avoid any kind of heat transfer problems, it is necessary to use special tank with a very low conductivity but also isolated to radiations. This is possible but even if this method allows to store two or three times more hydrogen than compressed hydrogen method in a specific volume. Indeed, the volume needed to store approximately 5kg of hydrogen would be of 71L. [4] Nevertheless, this method has some drawbacks. It requires a lot of energy and

then increases a lot the energy consumption. Furthermore, there is still a heat transfer even if the hydrogen is stored in a high adiabatic system, then it increases a lot the pressure. This could create some safety problems due to a too high pressure, then it is necessary to use safety valves which help to release the gas excess created by the heat transfer. Finally, as it is said before, the consumption of energy to keep the hydrogen at the liquefaction point limits the possible use of this method for a daily use as for hydrogen cars, indeed the cost is so high in terms of energy that this method could only be used for aerospace applications where the cost is not so important. [6][7]

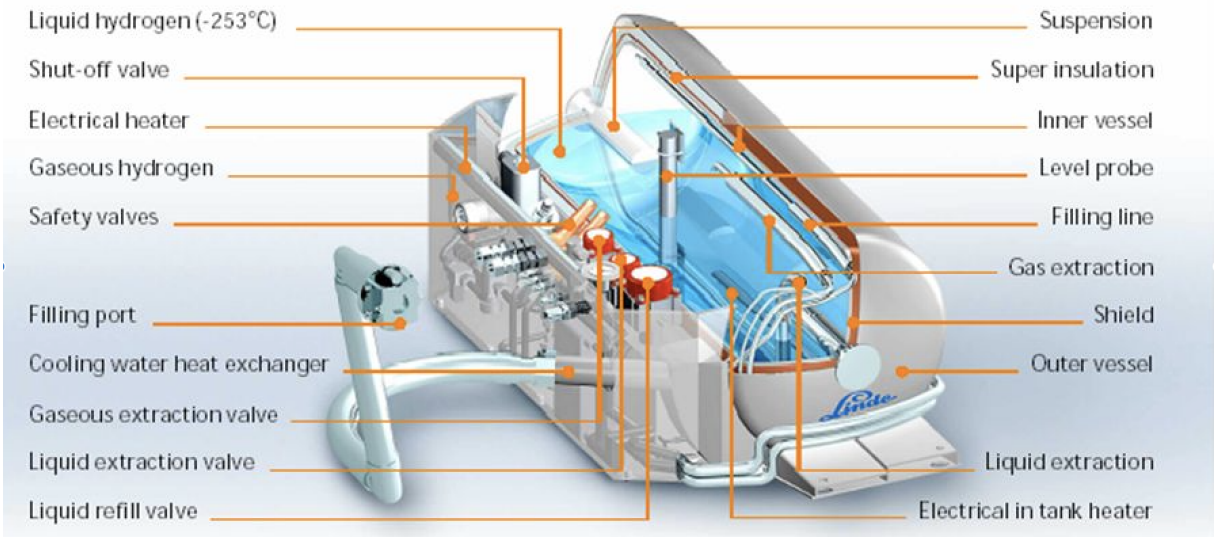

Figure 2 : Liquified hydrogen tank[8]

1.2.3. Solid hydrogen storage

In order to manage the different problems due to the liquified or compressed hydrogen storage, especially in terms of energy and safety, another solution is possible. Indeed, it is possible to store solid hydrogen. The aim of this method is to combine chemically or physically the hydrogen with the materials from the tank in order to get hybrids.

Indeed, hydrogen reacts at elevated temperatures with many transition metals in order to create hybrids. Then the hydrogen could be stored or release when required by using different methods as a thermal stimulation or hydrolysis.[9]

Concerning physisorption, as hydrogen is a gas, this phenomenon is also there. Indeed, due to the Van der Waals forces, the hydrogen will be attracted to the surface without dissociating. Nevertheless, this interaction has a low strength, indeed, the enthalpy of this reaction is between 4 – 10 KJ / mol. That is why, to get an important physisorption it is necessary to have very low temperatures. As physisorption occurs on the surface, having a high specific surface

area increases a lot the phenomenon. In order to increase the rate of physisorption many nanoporous materials were created as carbon nanotubes. [10]

The chemisorption is another phenomenon which occurs when the hydrogen comes in contact with the metallic surface. Indeed, the hydrogen will dissociate and split into two new hydrogen atoms which will penetrate the material by diffusion and create some new bond with it.[11] Furthermore, this phenomenon is totally reversible which is a great advantage. Indeed, the metal alloys can absorb the hydrogen and then release at some temperatures in order to recreate hydrogen. This is mainly why solid hydrogen storage could be one of the most important solution in the future [6], it helps to store hydrogen with safety while storing it using compressed or liquified solution could create some safety problems. The temperatures and pressures used for this kind of storage are way smaller than for the other kind of storage. What is more, metal hybrids created by this method have a way higher capability of storage. Considering all these advantages, it seems like solid stage storage of hydrogen could be the most interesting way to store hydrogen in the future, especially with a high safety for daily use as cars tank for example. [12]

1.3. Metal hybrids

Considering the use of metal hybrids, hydrogen storage could be improved a lot. Indeed, hydrogen could be absorbed and desorbed just by changing temperature and pressure in a system. The reason of this is the chemisorption, indeed with a metal, the hydrogen will create some new metallic bonds and create a metal hybrid. It is important to notice that in the metal hybrid, hydrogen act as a metal and create some metallic bonds. [9] Nevertheless, metal hybrids have some drawbacks, one of the main is the oxidation. Indeed, the surface of the metal will be covered by a oxide layer which will reduce a lot the hydrogen absorption acting as a hydrogen barrier. In order to reduce this phenomenon, it is necessary to work under a protected atmosphere after having break the oxide layer. In order to break this oxide layer, it could be useful to use for example a planetary milling and then work in a protected atmosphere.[13]

In fact, the hydrogen just sits on the interstitial sites of the metal structure. Considering M as a metal, most of the hybrids created are from this type: MH , MH_2 , MH_3.

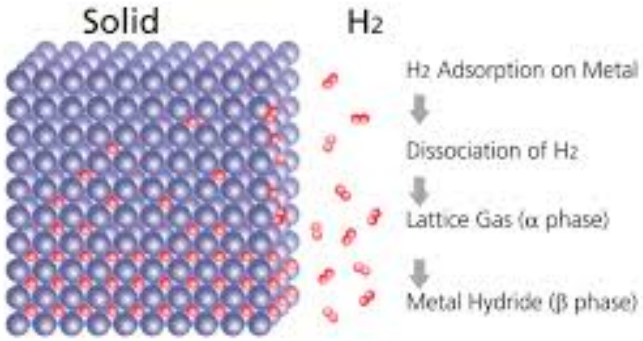

Figure 3: Formation of metal hybrids[14]

Considering all these points, it is possible to divide the metal hybrids in two different parts which are the high temperature metal hybrids and the low temperature hybrids.

1.3.1. High temperature metal hybrids

These metals have high absorption and desorption properties but low kinetics properties.
Most of these metals are very light and have a great absorption capability.
Magnesium is the most common used metal for metal hybrid used for storage of hydrogen[15], [16], [17]. Indeed, it has a very high storage capacity of 7,7 % wt. Furthermore, it has also the advantage of being very abundant on earth while other metals as Palladium could be very efficient but are not abundant at all. [18], [19]Although MgH2 has some drawbacks which are the kinetics properties, the decomposition, absorption, desorption, which are really slow. In theory this is not so problematic, but considering daily use in applications as cars, this is very problematic.

1.3.2. Low temperature metal hybrids

These metal hybrids are the opposite of the first category; indeed, they have low absorption and desorption properties but really high kinetic properties. The main problem of this category of metal hybrids is the metal required to form these. Metals needed are mainly some rare earth or really expensive and rare metals. This problem limits a lot the use of these materials for daily application. Nevertheless, these materials are very interesting to store hydrogen but the quantity of hydrogen that they can absorb is very low if we compare it to Magnesium for example.

Considering all of these, this is possible to use alloys in order to improve the characteristics as kinetic and temperature ranges of absorption. To do this, many researches are carried out. Indeed, it is possible to alloy them with other metals or even use the mechanical milling which will help to change the structure of the metal. It is also possible to dope these metals with other components. As an example, FeTi [20]has been tested many times but the main problem of this one is that the oxide layer created by the titanium is really hard to break and then is a real limit for the hydrogen absorption. Nevertheless, the quantity of hydrogen they can absorb is still quite low. To improve this quantity, it is necessary to get the right stochiometric proportions using phases diagram.

Another solution could be using MgTi [21] which would be part of the study of this internship. Indeed, it could be an alloy which combine good kinetic properties but also a good range of temperature for absorption and desorption.

1.4. How to determine the hydrogen storage capacity ?

In order to determine the hydrogen storage capacity, the most common method used is the Sievert's method. With this method, it is possible to determine the kinetic and absorption properties.

This method consists in a measure of pressure. Indeed, the pressure is measured in a tank of a known volume. Then the hydrogen is put in the system and then enter in contact with the material tested. The temperature will be controlled and increase in order to reach the equilibrium. Finally, the pressure will be measured again in order to determine the difference of pressure between the beginning and the end. Then it is possible to determine the number of moles absorbed by the material using PV=ZnRT.

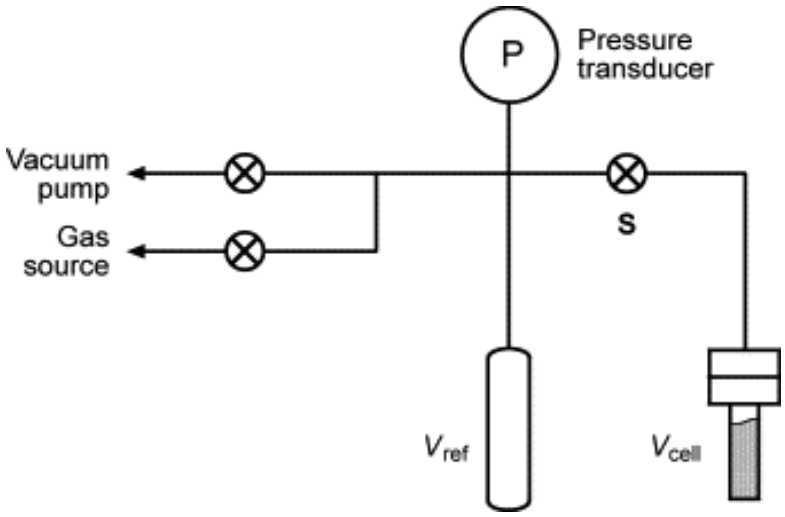

Figure 4 : Sievert's method illustration[22]

This method is the most common used by the lab working on hydrogen absorption. Some machines have been developed in order to get accurate results concerning kinetic properties. An example of machine using Sievert's method could be the PCTpro created by SETARAM. Indeed, it allows to determine the kinetic and absorption properties of a material automatically.

Figure 5 : PCTpro by SETARAM[23]

1.5. Optimization of materials properties

In order to optimize the absorption of hydrogen, it is necessary not to have an oxide layer. Furthermore, reducing the size of the particles of a material helps to create more specific surface area and then improve hydrogen absorption. Moreover, the more the material has defects, the more it will absorb hydrogen. Then, to optimize absorption of materials it is also possible to create some alloys by mixing different powders. Indeed, using mechanical milling help to break the agglomerates of powders and decrease significantly the size of the particles by hitting the walls of the vials with the balls of stainless steel.[24] Furthermore, the increase of the hydrogen absorption capacity is due to the increase of the porosity which helps to get a better hydrogenation as the increase of defects and surface area.[21]

To do this, mechanical milling is a solution. Indeed, it helps to reduce the particle size and to harden a material using the plastic deformation. Moreover the milling also help to create some stacking faults and get a stabilized structure (for alloys for example) which will help to increase the hydrogen absorption.[25]

This method consists in putting a metallic powder in vials with metallic balls. By rotating, the balls will hit the walls of the vials and reduce the particle size of the material. The impact and friction effects will also introduce severe deformation. By using this milling method, it also breaks the oxide layer which is a barrier to the hydrogen absorption.[26][27]
The vials are place on a base which is rotating at the speed chosen during the parameter's choice.

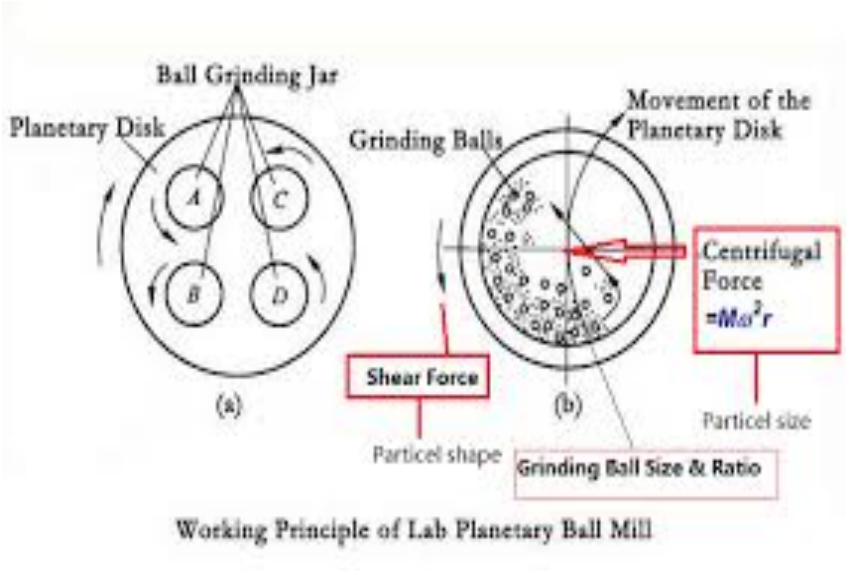

Figure 6 : Working principle scheme of planetary ball milling[28]

In order to obtain the optimal material after the milling, there are many parameters which are important to choose.

Vials:

To avoid the contamination of the powder by the material of the vial it is necessary to choose the right material. Furthermore, the shape of the vial is important to maximize the impact of the ball against the walls and then the powder. Most of the time, stainless steels, hard metals or ceramics are used.

Milling balls:

Commonly, the balls are in the same material as the vials to also avoid contamination of the sample. It is also possible to choose the size of the balls, indeed, the smaller the balls are, the higher the friction is while bigger balls increase the energy exchange.

Milling speed:

By using higher speed, more energy will be transmitted to the powder, but cold welding could occur on the walls of the vials and the milling balls. Increasing the milling speed will also increase the friction and the amount of impact and then increase the temperature reached.

Time:

One of the most important parameters remains the milling time. Indeed, increasing the milling time will also increase the energy and the impact and then the deformation.

Powder/ball weight ratio:

Increasing this ratio will also increase the energy transmitted to the powder, indeed the number of collisions between the powder, the balls and the walls of the vials. Nevertheless, it is important not to have a too high ratio in order to let the movement of the ball be complete in the vials during the milling. But, increasing this parameter allow to reduce the milling time.

Control agent:

During the milling, adherence between the powder, the balls and the walls could be created. This is why it is necessary to use a control agent which could be liquid or solid in order to limit this adherence. It helps to reduce the friction and the cold welding. Furthermore, it is necessary to choose the good one and also the good quantity in order not to contaminate the sample with this agent and not to reduce too much the deformation occurred by the milling.

Atmosphere:

This parameter is also very important to avoid the oxidation of the samples. Indeed, using a protective atmosphere helps not to create the oxide layer which would be the limit to use the sample for a hydrogen storage. Indeed, the temperature created by the friction and the impact inside the vials during the milling will accelerate the oxidation and using a specific atmosphere is vital.

Finally, by selecting the parameters, it is possible to increase the number of defects on the surface of the sample and then increase the hydrogen absorption. Moreover, it helps to break the oxide layer which could be created. Then using this method before testing the absorption of the metal is essential to get good results.

2. Objectives

The final aim of this project is to find some metallic hybrids which have good properties concerning hydrogen storage capacity. It means, good absorption and desorption properties. To do this, it is necessary to use mechanical milling in order to improve the material properties as it is explained in the first part.

Then, the second aim of this project is to study the structural changes observed by different characterization techniques after mechanical milling of the different compounds and try to relate them with the observed behaviour in hydrogen tests.

After reading literature, the first metal chosen was Magnesium. Indeed, this material is very abundant and so have a low price which is very important in order to develop the hydrogen storage for daily uses. Furthermore, this metal has very high hydrogen absorption properties thanks to its structure.

Then, the second material chosen was a mix of Magnesium and Titanium (2/3 of magnesium and 1/3 of titanium). Indeed, mixing these two powders could help to improve the range of temperature where absorption is important for the magnesium while keeping the really high hydrogen absorption properties of the magnesium.

Finally, the third mix which was chosen is Magnesium, Titanium and Iron (4/6; 1/6; 1/6 respectively) in order to still improve the range of temperature when hydrogen absorption occurs while keeping some good kinetic properties of absorption/desorption.

The use of mechanical milling helps to create some nano powders of metal. It helps to improve the hydrogen storage properties by improving the surface area, the particle size but also by breaking the oxide layer which is a barrier for the hydrogen absorption. By using the mechanical milling, it also helps to create homogeneous mix of the metal powders.

After obtaining these powders, it was necessary to test their hydrogen absorption properties but also their kinetic properties using the Sievert's method. To test these properties is it necessary to be in a protected atmosphere in order not to let the oxide be created on powders.

3. Experimental procedures

In this part of the report, the procedure used for all the experiences will be described. Also, the parameters chosen for the development of the metallic hybrids created with powders.

3.1. Development of metallic powders

3.1.1. Mechanical milling

The machine used for the mechanical milling was a Pulverisette 5 type planetary from the company Fritsch. The vials used for the milling were two stainless vials (AISI 304) with a 250mL capacity.

Figure 7: Planetary ball milling machine (Pulverisette 5)

Concerning the balls used in each vial, it was tempered stainless-steel balls with a diameter of 10 mm and a weight of 4,1g. The powder-ball ratio used for each milling was the same, 19,8:1. By using a powder-ball ratio as this one, it manages the problem of an excess of energy created in the vial, but it is still assuring a good deformation of the metallic powders. For each milling,

6 grams of metal powder and 29 balls were put in each vial with 4 mL methanol which is the agent avoiding the dryness and the stickiness of the powder.

Furthermore, it is important to do the milling in a protected atmosphere in order not to create the oxide layer during the milling but also for safety because activated magnesium could explode. That is why, the vials were closed in a Glovebox from Plas Labs to manage the problem of the protective atmosphere. At the end of each milling, the metal powder was stored into glass vials which had to be sealed with Parafilm.

Figure 8: Vials used in the Pulverisette 5

3.1.2. Magnesium milling parameters

First, it is necessary to choose the parameters of the milling. For all the milling done, only one parameter will change, the milling time.

The control agent chosen was liquid methanol, the milling speed chosen was 160 rpm. This speed is optimal in order to reduce the cold welding and then not have a contamination of the sample due to the material of the balls or vials. Furthermore, the temperature inside the vials during the milling has to be controlled, that is why it is necessary to do cycles of 30 minutes milling and 30 minutes break until we milled the necessary number of hours. Indeed, a too high temperature could be obtained during the milling due to the energy from the friction. Then, it is also necessary to be in a protective atmosphere as it is mentioned before. Indeed, the milling increase the specific surface of the powder and make the powder very explosive

and the magnesium could flame spontaneously. This is why it is also to empty the vials in the glove box in order to avoid any combustion of powder. Concerning the milling time, for the experiences, the milling time chosen were 1, 2 and 4 hours.

3.1.3. MgTi milling parameters

As for the magnesium, the parameters for the milling has to be chosen. The only changing parameter is still the milling time.

For this milling, 2g of fine titanium powder and 4g of magnesium powder were put in each vial with 4mL of methanol. Still, the vials were closed in the glovebox in order to get a protective atmosphere. The experience was led with three different milling time of 1, 2 and 4 hours.

3.1.4. MgTiFe milling parameters

For this material, the mix chosen was 1g of fine titanium powder, 1g of iron powder and 4g of magnesium in order to preserve the good hydrogen absorption properties of the magnesium. Concerning the milling parameters, it is still the same as for the two first powder's mix. Nevertheless, for this material the only milling time used was 1h.

3.2. Mechanical milling and glovebox procedures

In order to make the experiment, it is first necessary to develop the fine metal powders. Then to do it, it is important to respect a strict protocol to protect the powder from the atmosphere. With this process, the errors will be minimized, and the powder will be protected from the oxidation.

Figure 9: Glovebox from PlasLabs

For the magnesium, 6g were weighted two times in a calibrated scale. Then it was introduced in each vial with 4 mL of liquid methanol measured with a burette. Then the vial, the lid and the support are put in the chamber of the glovebox in order to make vacuum before closing the vial.

The procedure to follow is very strict and is necessary in order to preserve the samples from oxidation. First it is necessary to close the inner door and the outer door of the vacuum chamber. This chamber has 2 valves which are respectively connected to a vacuum pump and to a nitrogen source. Then, the vacuum valve has to be open and the vacuum pump activated until 20 inches of Hg in VAC. Right after, the vacuum valve is closed and the nitrogen one is open in order to vacuum chamber until we reach atmospheric pressure. To be sure that there is no oxygen in the chamber, this operation is repeated 3 times before opening the inner door and introducing the vials into the glovebox.

Figure 10: Vacuum chamber of the glovebox

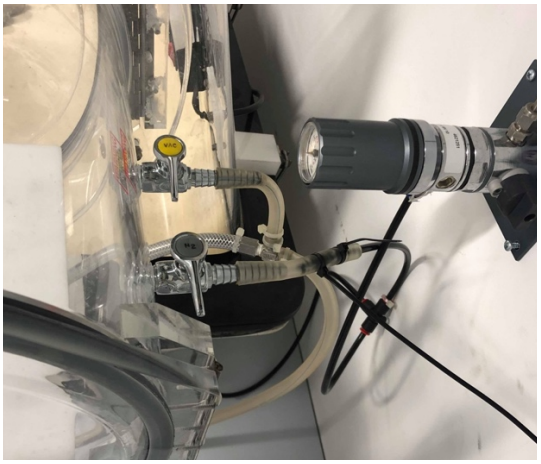

Figure 11: Valves used to make vacuum inside the chamber

Once the vials and the Allen key are in the main chamber of the glovebox, the vials are closed as much as possible in order to get a protective atmosphere in the vials.

Finally, the vials are extracted by using the secondary chamber, first by open the inner door with the outer door closed and then close the inner door to finally open the outer door and extract the vials in order to put them in the planetary milling machine.

The closed vials are then placed in the Pulverisette 5 type planetary milling machine. Then we select the parameters wanted on the electronic panel. In order to avoid problems during the milling, it is necessary to screw very toughly the vials and put them symmetrically in the machine.

After the milling, it is necessary to empty the vials, but it is still necessary to do it in the glovebox. Furthermore, it is especially necessary in this case because of the activation of the powder. Indeed, the powder is highly activated and could burn spontaneously if there is a contact with oxygen. Then, the vials are put in the secondary chamber with a glass vial, a satin paper, a hammer, a beaker, a spatula, a hammer, a parafilm and an Allen wrench. Afterwards, the procedure described before is done again in order to work in a protected atmosphere in the glove box.

The procedure to extract the powder from the vial is the following one:

First, the vials are open with the Allen wrench, then if there is too much vacuum, in order to unstick the lid of the vial, it could be necessary to hit the vial with a hammer. Then, it is necessary to scratch the top of the vial using a spatula in order to get the powder stuck to the lid. With the help of the spatula, the 29 balls of each vials are extracted in the beaker. After this, the beaker is shake in order to unstick the powder from the balls. Then the powder in the vials is emptied on the satin paper. Afterwards, the powder is put in the glass vial and the glass vial is closed and sealed by parafilm.

Once this procedure is ended, the vials and the glass vials sealed are extracted from the glovebox using the same procedure as usual. Some silica sand is right beside of the glovebox in order to extinguish a metallic fire due to the rest of powder in the vials. Then the glass vial is marked with the composition of the powder, the amount of methanol used, the cycle used for the milling (30/30 in our case), the milling speed but also the milling time.
Afterwards, the vials, the balls are cleaned using ethanol, ultrasounds and paper in the sample preparation room and put in the light process laboratory.

3.3. Scanning electron microscope (SEM)

In order to characterize the samples, scanning electron microscopy (SEM) could be used. The principle of this method is to produce an image of the sample by scanning the surface of the sample using a focused beam of electrons. The beam is focused through an electromagnetic lens. Then, the interaction between the sample and the electron will send back to the user many information about the external morphology and the chemical composition. (Very useful in our case to see if there is a contamination by the vials and balls).

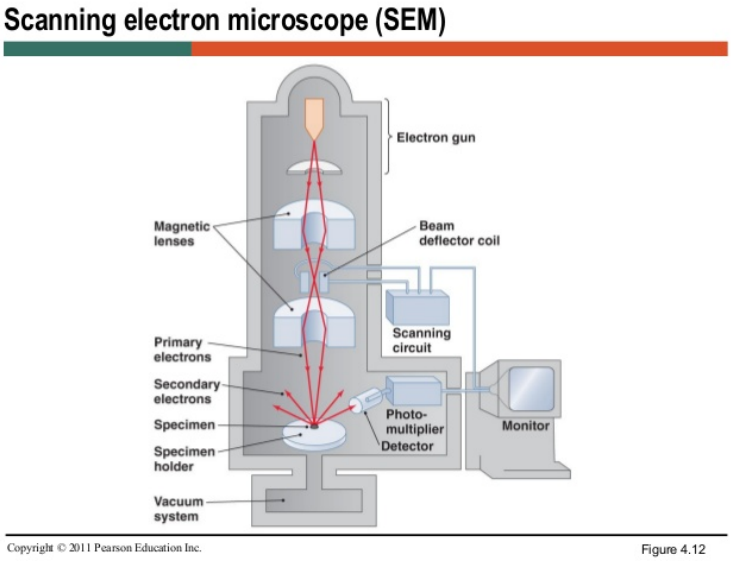

Figure 13: Scanning electron microscope illustration[29]

The information obtained are due to the impact of the electron with the sample, indeed, the electrons are accelerated and so have a lot of kinetic energy. This is the energy which will give back a large range of signals by decelerating when hitting the sample. For example, we can obtain information using the secondary electrons but also the backscattered.

The different signals produced can provide information about different things. Indeed, the secondary electrons are used to get information about the morphology and the topography of the sample because the signals come from the surface of the sample while back-scattered electrons are used to identify the different element present in the sample. (Especially useful in our case to identify the different element for a mixed powder)

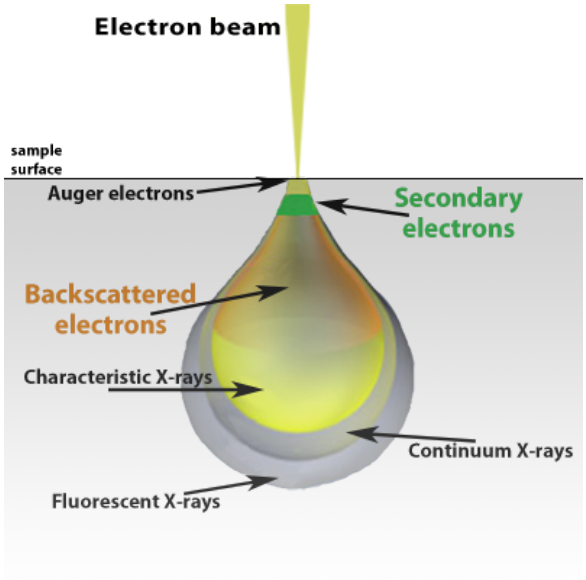

Figure 14: Different signals produced[30]

The powders that we obtained with our milling were so analysed by the scanning electronic microscopy. In order to analyse these samples, it is first necessary to put a bit of powder onto a double-sided tape and put it in the machine. Some images were taken at different magnification, 150x, 1000x, 5000x but also 15000x. Furthermore, to see if contamination happened between the vials, the balls and our powders, an EDX was made to determine the different element.

3.4. X-ray diffraction

In order to analyse the different crystalline phases of sample, x-ray diffraction could be used. This method is based on interference between a single wavelength x-ray and the crystalline sample. The x-rays are created by a cathode ray tube, filtered, concentrated and sent to the sample. The interaction created will produce some interferences and a diffraction.
To use these data, the Bragg's Law will be used ($n\lambda=2d \sin \theta$), which will allow us to determine the lattice spacing in the crystalline sample. Then, considering this, the different minerals are identified by using the references of the lattice spacing.

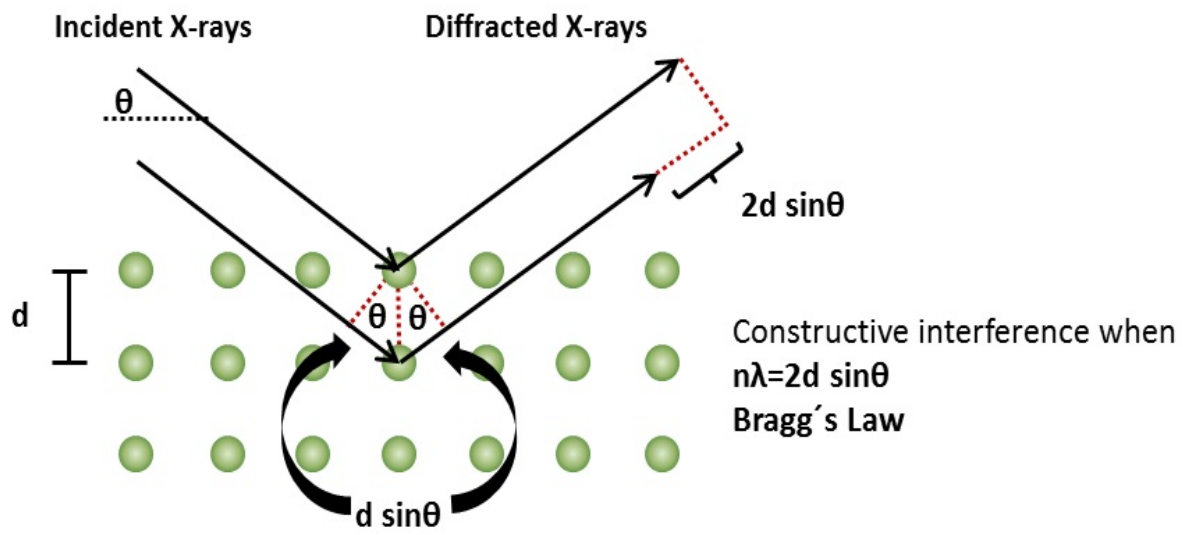

Figure 15 : Scheme of the x-ray diffraction[31]

Using this method, information were obtained about the composition, the size and the texture of all our samples and especially for the powders of MgTi and MgTiFe.

3.5. BET tests

In order to make measurements about the specific surface area of a powders. A method called BET (Brunauer, Emmet and Teller) can be used. This method evaluates the amount of gas adsorption and then gives a result about the specific surface area in area per mass of sample. First, the sample is "cleaned" by remove all the impurities on it. To do this, the process "outgassing" is used. The sample temperature is increased while there is a flow of vacuum or inert gas on it.

Then, using physical adsorption with a gas (which depends on the powder analysed). Afterwards, the amount of gas adsorbed is calculated and finally, the specific surface area is also calculated considering a monolayer formation as on the following scheme.

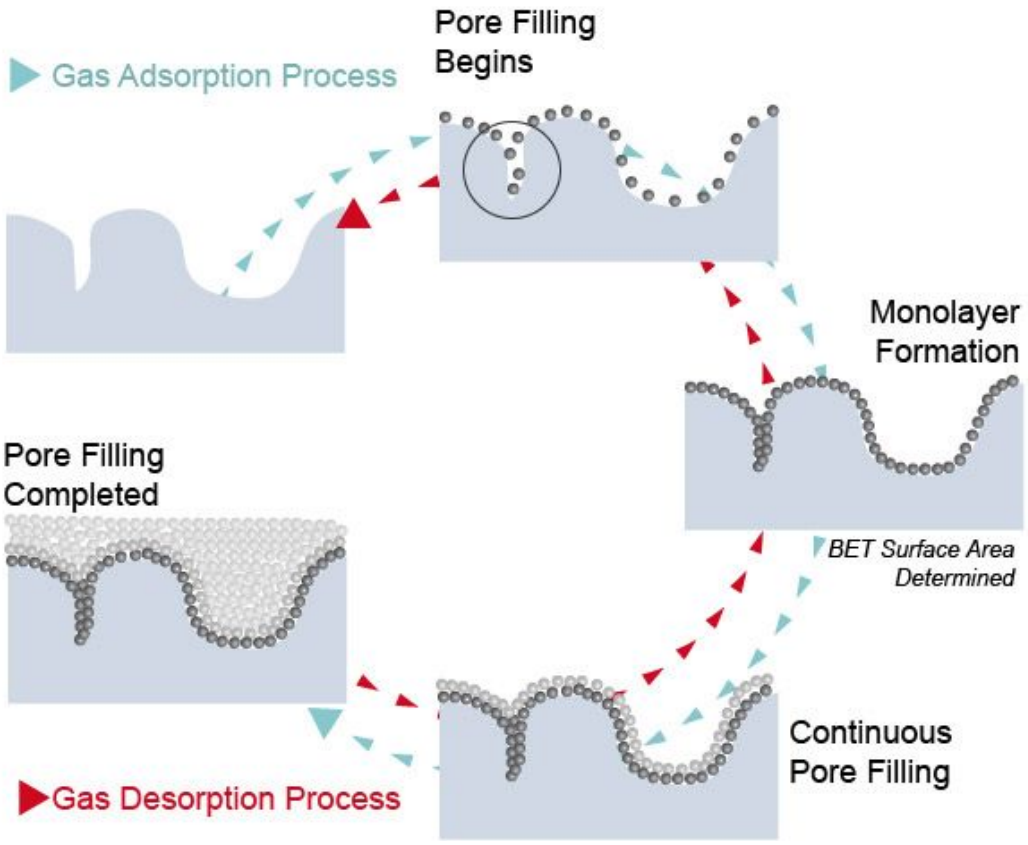

Figure 16: Scheme of the BET process[32]

3.6. Particle Size Distribution

To understand well how the powder is composed, it is also necessary to measure the particle size distribution. It corresponds to a list of values which define the number of particles of different size, mass and volume.

In order to understand the behaviour of our different powders, PSD was measured for each sample.

The measurement of the particle size distribution was done thanks to a LS 13320 Beckman coulter LS particle size analyser. This machine used the laser diffraction in order to calculate the particle size distribution. It is calculated by measuring the angle of light scattered by the particles as they pass through a laser beam. The analyser has many different light detectors in order to get precise data. Thanks to this method, the particle in the range of 10nm to 3mm can be detected which is the right range for our experiments.

Figure 17: LS 13320 Beckman coulter used for PSD[33]

3.7. Hydrogen absorption equipment

To test the hydrogen absorption, the equipment used was created by the last student who worked on this subject. The method used is based on the Sievert's method. Thanks to this, it is possible to know more about the absorption/desorption kinetic properties of each powder. The equipment used has 2 different parts, the first one is composed of the hydrogen bottle, a pression reducer, pipes with different valves in order to make vacuum inside of the system but also a temperature controller and some sensors linked to an Arduino card and be able to get the data of the pressure during the whole experience. The second part of the system is a tank which is able to resist to high temperature and high pressure, this tank will contain the powder which has to be tested, furthermore this tank also is plugged to a thermocouple which allow to obtain the temperature during the test.

Figure 18: Picture of the whole system without the tank and picture of the tank

3.8. Hydrogen absorption testing

First of all, it is necessary to test if there are any leaks in the system in order to not have a pressure leak which could create false data and then ruin our test.

To do so, the tank is plugged on the system (with its valve closed) without any powder inside, in order to not waste powder if there is a leak. Then, the vacuum is made inside the system using 2 valves linked to argon gas and a vacuum pump. The middle valve has to be open and the hydrogen valve has to be close as the tank one. Then the vacuum valve is opened, and the vacuum pomp started. Afterwards, argon gas valve has to be opened with a flow of 2 bars (while vacuum one is closed). Finally, the vacuum is made until we reach 2,5e10-1 mBar. This process is repeated 6 times in order not to have some oxidizing gazes inside the system.

Afterwards, the hydrogen is released into the system at 20 bars thanks to the pressure reducer, and the valve of the tank is opened. Then, the pressure is controlled for 10 minutes thanks to an Arduino UNO Card linked to a laptop and a program.

Figure 19: Valves used to make the vacuum inside the system

During many trials, the system had some leaks which not allow to get some proper data about the hydrogen absorption. To detect the problem in the system when there is a leak of hydrogen, it is necessary to put some soap at all the joints and valve. Indeed, if there is a leak at a point, the gas will blow and then create some soaps bubbles at the joint.

Most of the problem were localised on the tank. Although the tank was well screwed, some gas leaked due to many problems. First, the joint used on the tank didn't fit the joint from the pipe well. Then it created some leaks of pressure. Afterwards, the joint of tank was changed but had to be shaped many times at the exact same size of the pipe.

When no leaks are detected, the real hydrogen absorption test can begin. To do so, the tank is filled in the glovebox with 1,5g of powder which is also weighted inside the glove box thanks to a scale introduced with the powder vials and the tank in order not to create an oxide layer. For this step, the procedure used is still the same, to avoid oxygen to enter into the glovebox. Before getting the tank out of the glovebox, it has to be screwed as much as possible. Afterwards, the tank is also screwed on the workbench because it is easier than in the glovebox.

Once the tank is ready and well screwed, it is connected to the system with its valve closed, and the process to make vacuum inside the system is repeated. The program which collect temperature (Picolog 2) and the pressure (Arduino) are launched and the test can begin.

```
float pres = 0;
int temps=0;

void setup() {
  // put your setup code here, to run once:

Serial.begin (9600);
}

void loop() {
  // put your main code here, to run repeatedly:
int valor = analogRead (A0);
float pres = (valor-100)/14.1;
int temps=(millis()/1000);

 Serial.print(temps);
 Serial.print("     ");
 Serial.println(pres);
  delay(1000);
}
```

Figure 20: Program used in Arduino to get the pressure

To start the test, the temperature controller is set on the wanted temperature and then increase in a constant ramp. Tests were carried out at a temperature of 250°C during 1 hour after reaching this temperature. Finally, the data are collected and put in an excel in order to plot the graphs of the time versus the temperature and the pressure.

The pressure is decreasing as the hydrogen is absorbed by the material tested. Indeed, the pressure created by the hydrogen take less volume while it is absorbed and then make the pressure decrease. In order to get the percentage of hydrogen absorbed, is it necessary to make some calculation thanks to the data we collected by using Excel. First, the graph of the pressure, and the temperature are plotted in function of the time.

27,23	816	254,463
27,23	817	254,51
27,23	818	254,561
27,23	819	254,613
27,23	820	254,652
27,23	821	254,704
27,3	822	254,758
27,23	823	254,803
27,3	824	254,837
27,23	825	254,869
27,23	826	254,91

Figure 21: Tables of pressure, time and temperature

Then, the number of moles absorbed can be calculated using the equation: PV=ZnRT Considering that we know the pressure, the temperature, the gas constant and also the volume of the system which is: 0,00001948 m^3. By calculating Z, the compression factor using a linear regression with the thermodynamics data that could be found in the literature easily. Afterwards, the mass of hydrogen absorbed is calculated using n=m/M. Finally, we can obtain the percentage of the hydrogen absorbed: $\%H_{2abs}$=m/1,5g.

4. Results and discussion

The aim of this chapter is to introduce all the results that have been obtained during the whole project. First, the characterization results will be presented in order to determine the different morphology of the powders used for hydrogen absorption tests. Afterwards, the results of hydrogen absorption will be presented. Finally, the aim is to find the relation between the morphology and the absorption for the different samples considering the different parameters used for the mechanical milling and the composition of the powders.

4.1. Metal powder morphology

Three different composition of powders were studied, first, only Magnesium, then Magnesium and Titanium and finally Magnesium, Titanium and Iron mixed. Each of these different mixes has been milled for different times. Magnesium was milled 1 hour, 2 hours and 4 hours, the milling time for the different samples of MgTi were the same. Finally, MgTiFe was milled for 1 hour only. In order to study, the morphology, the SEM pictures will be used. Different magnification (150x, x500, x1500, x5000…) were used on different places of the samples.

4.1.1. Magnesium powder morphology

Firstly, Magnesium morphology will be studied. There are 4 different samples of Magnesium. The first one is the initial Magnesium used for all the samples milled.

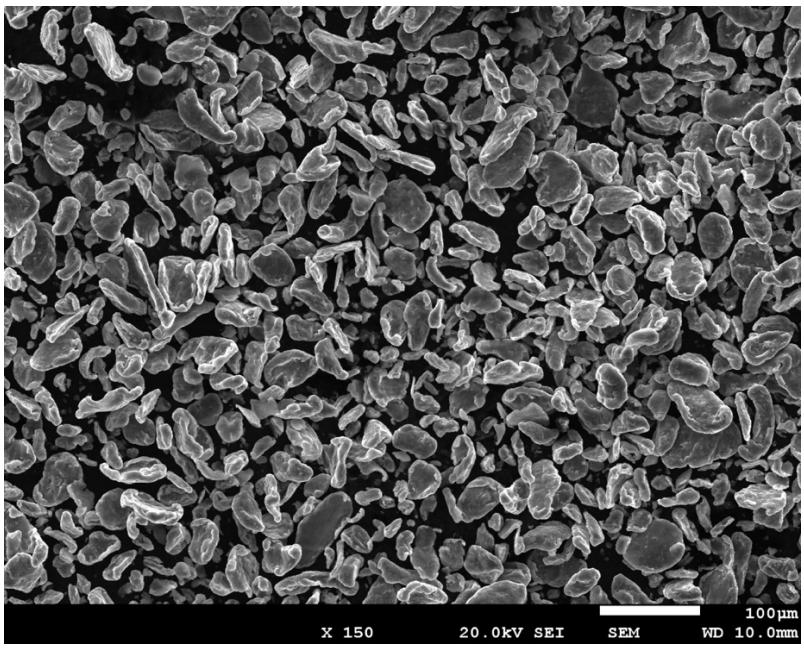

Figure 22: Initial Magnesium powder – SEM x150

On this first picture from the SEM at the magnification x150, the powder is quite thick and large because it has not been milled before. Considering the scale on the picture, the particles of the powder seem to have a size of 50 micrometres approximately. Nevertheless, this aspect of the particles will be treated in the PSD part. All the particles seem to be quite round, and non-deformed. With this magnification, it is not possible to see any kind of cracks on the initial powder. Moreover, it seems like there are no conglomerates of powder. In order to see more precisely the morphology of the powder, the same picture will be studied with a magnification of x500.

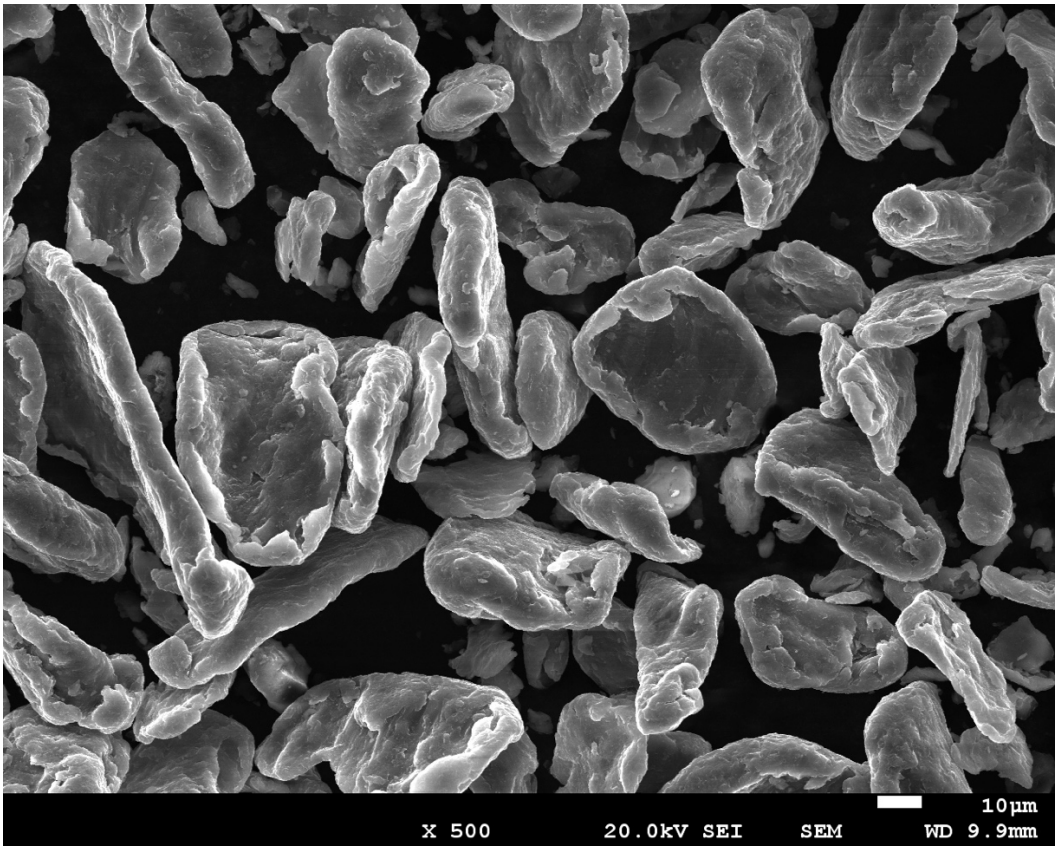

Figure 23: Initial Magnesium powder – SEM x500

On this figure, it is observable that there are clearly no deformations on the powder and no conglomerates of powder as it could occurs later as it will be seen with other powders.
Concerning the composition of the initial powder used for all the samples. As it is observable on the following figure, there is almost only Magnesium as it is specified on the bottle of Magnesium.

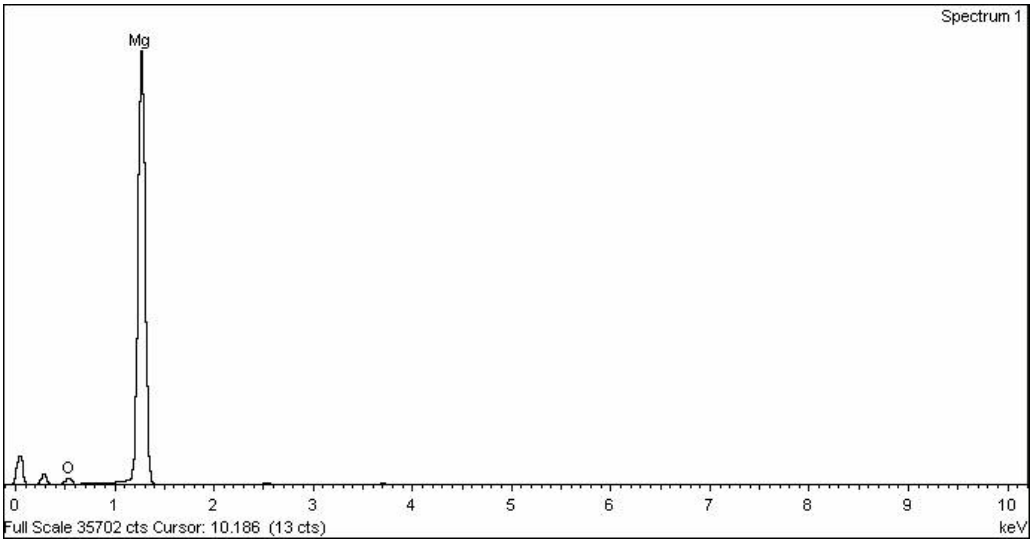

Figure 24 : Spectrum of initial Magnesium powder

Secondly, the following pictures will be about the Magnesium milled 1 hour with 4 mL of methanol as control agent.

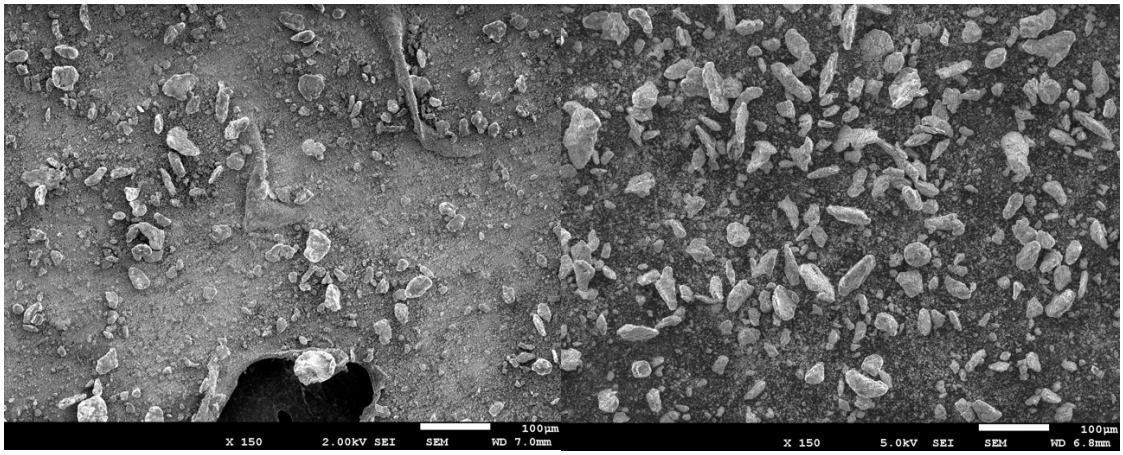

Figure 25 : Magnesium milled 1 hour with 4 mL of methanol – SEM x150

On these two pictures which has been taken at two different places on the sample, it is clear that the powder is totally different from the initial one. First, the particle size has been reduced a lot by the action of the mechanical milling. The size decreased from approximately 50 micrometres to approximately 20/30 micrometres for most of the particles (according to the scale). Furthermore, there are very small particles under the bigger ones. In order to see clearly how look the particles, the magnification has been increased.

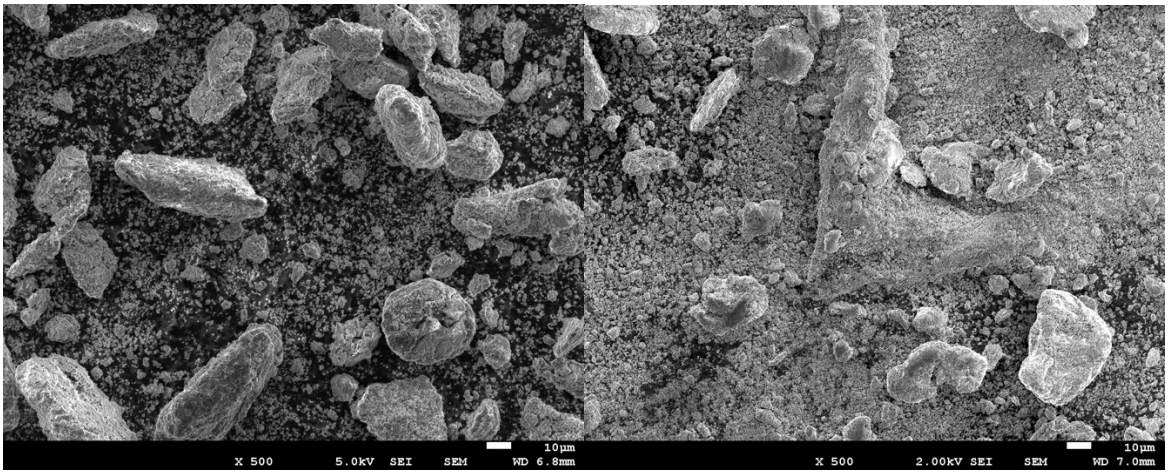

Figure 26 : Magnesium milled 1 hour with 4 mL of methanol – SEM x500

On these pictures, the smaller particles are really observable. Moreover, the bigger particles seem to have cracks which means that they had received mechanical deformation thanks to the mechanical milling as planned. Nevertheless, some particles seem to have agglomerates with other which could be due to the use of the methanol (which is the control agent).

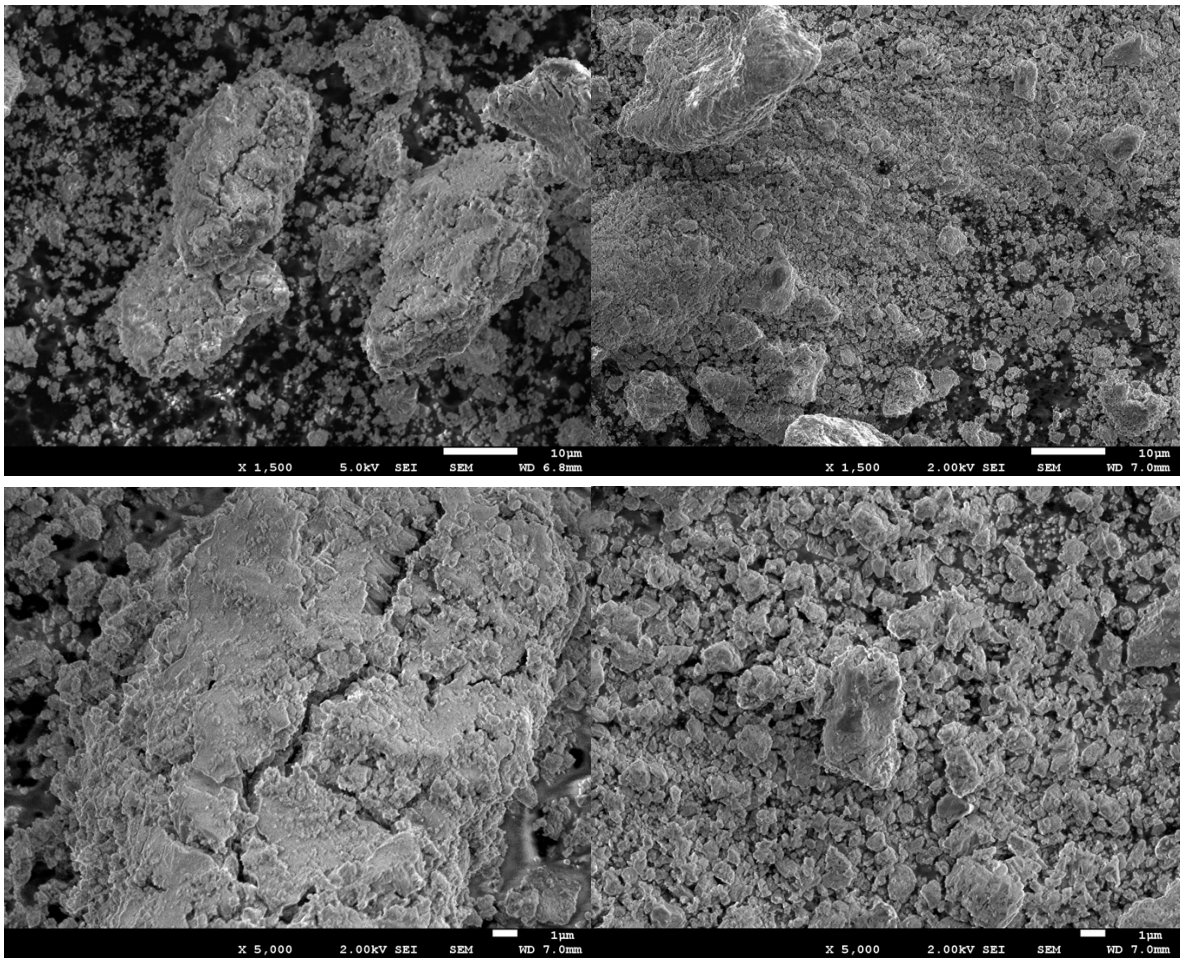

Figure 27 : Magnesium milled 1 hour with 4 mL of methanol – SEM x1500/5000

By looking deeper in the powder with magnification like x1500 and x5000, it is clearly observable that there are many cracks in the bigger particles and some of these particles seem to be conglomerate with others. The use of a longer milling time could maybe help to decrease the conglomeration but also reduce more the particle size.

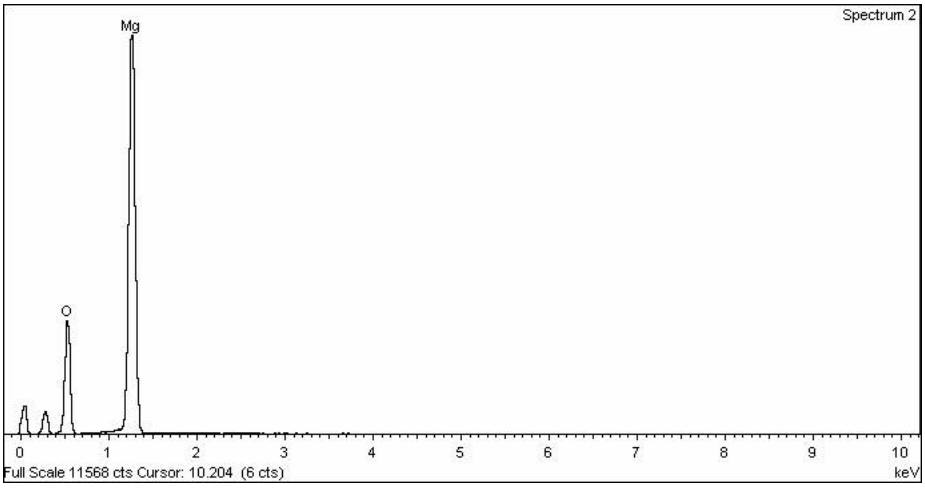

Figure 28 : Magnesium milled 1 hour with 4 mL of methanol – Spectrum

Concerning the spectrum, it doesn't change that much compared to the initial powder spectrum. Indeed, the 1 hour milling it not so long and then doesn't contaminate that much the powder with the stainless steel of the balls and the vials.

Thirdly, the following pictures will be from the Magnesium milled for 2 hours in the same condition as the first powder.

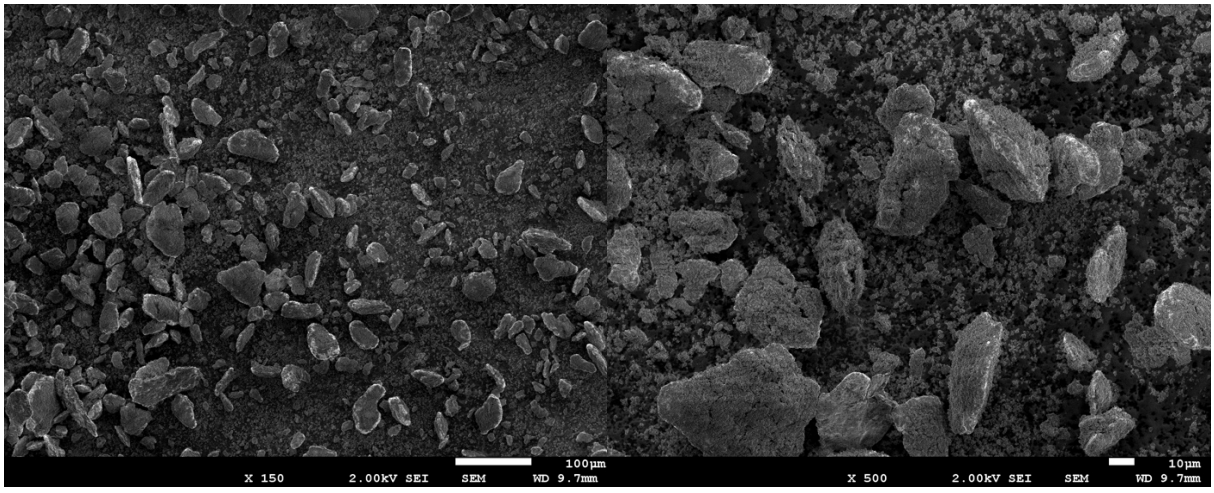

Figure 29 : Magnesium milled 2 hours with 4 mL of methanol – SEM x150/500

On these two first pictures, the powder seems to be thinner and less round than for the two first powder. Globally, even the bigger particles are smaller according to the scale and it looks

like there are less agglomerates than in the first powder. Nevertheless, it is necessary to observe the powder with a better magnification in order to understand the morphology.

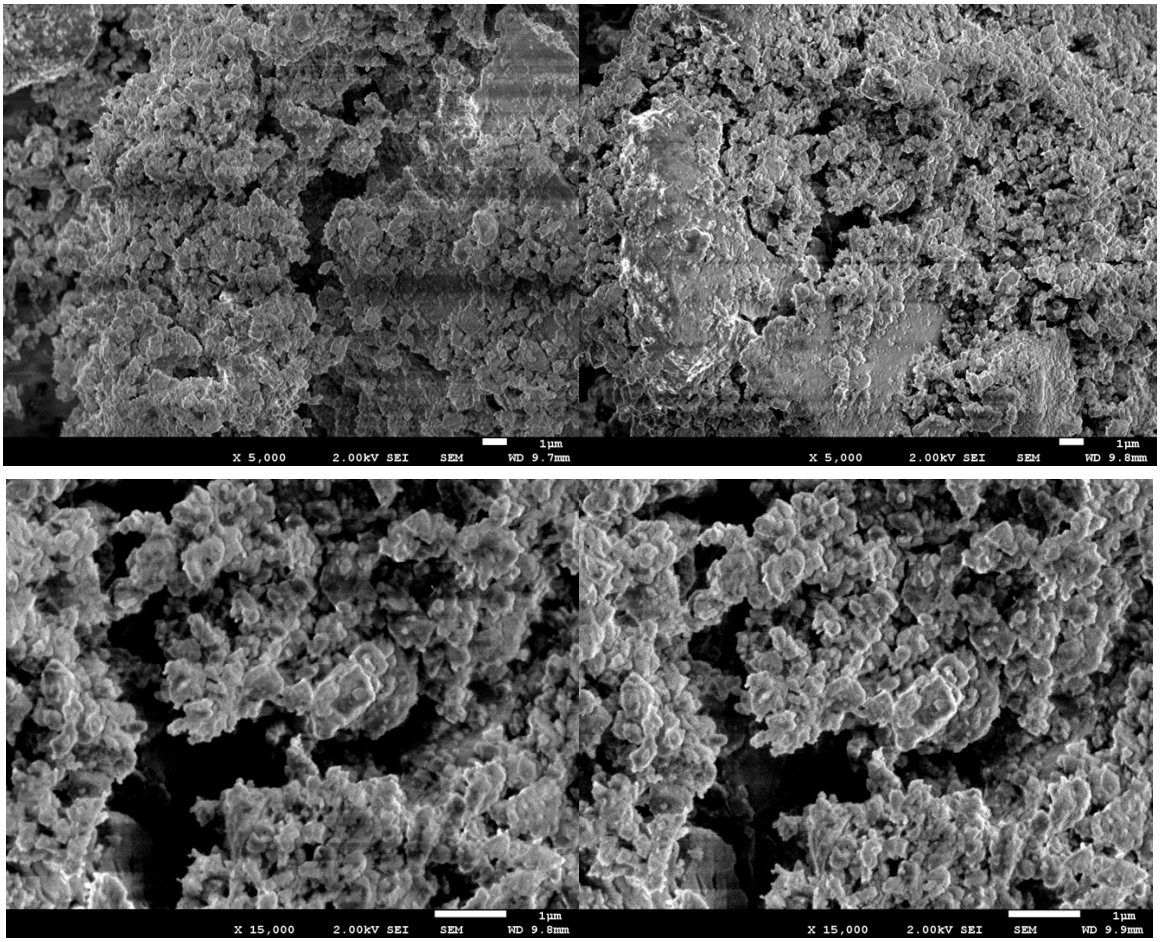

Figure 30 : Magnesium milled 2 hours with 4 mL of methanol – SEM x5000/15000

These pictures allow us to see clearly the fact pointed right before. Indeed, it is observable that there are many conglomerates and accumulation of small particles stuck with each other. Nevertheless, it also confirms the fact that the size of the particles has decreased compared to the first powder.

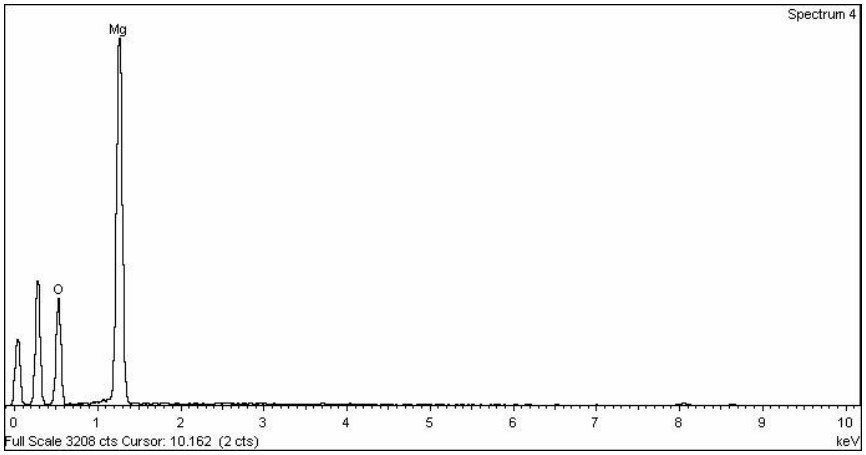

Figure 31 : Magnesium milled 2 hours with 4 mL of methanol – Spectrum

Concerning the spectrum, it is also almost the same as the previous powder, there are no significant changes which show a contamination by other metals.

Finally, the last Magnesium powder to study is the 4 hours milled powder.

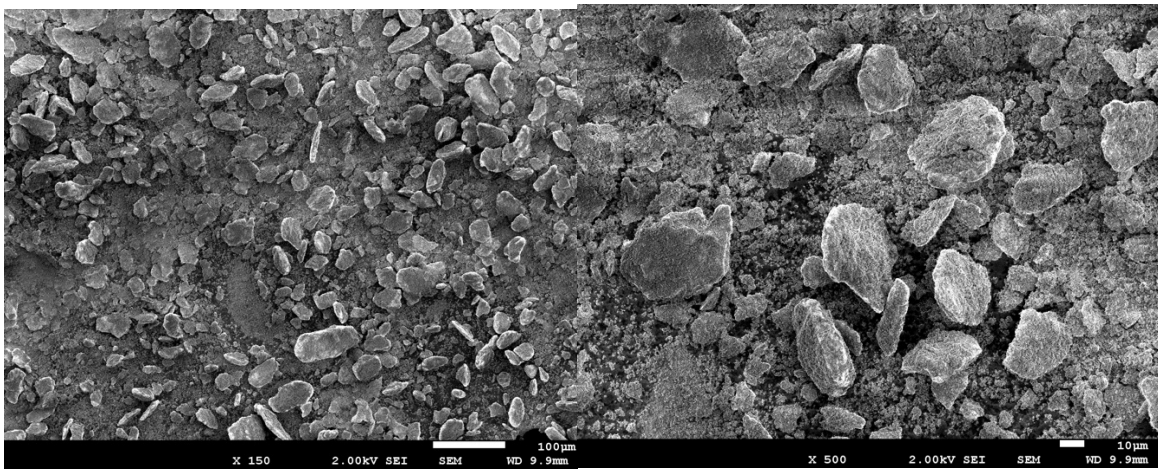

Figure 32 : Magnesium milled 4 hours with 4 mL of methanol – SEM x150/500

These two pictures of the powder milled 4 hours show us that there is no significant change at this scale. Indeed, the size of the particle is almost the same even if it is necessary to check it with the PSD test. Furthermore, the biggest particles on the picture with magnification x500 almost look like the one on the same magnification but for the third powder (Mg 2h).

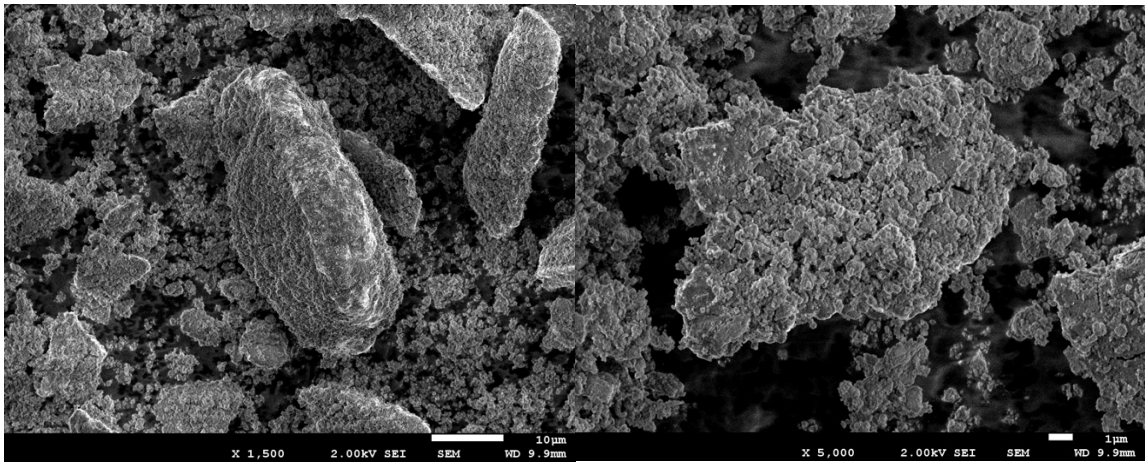

Figure 33 : Magnesium milled 4 hours with 4 mL of methanol – SEM x1500/5000

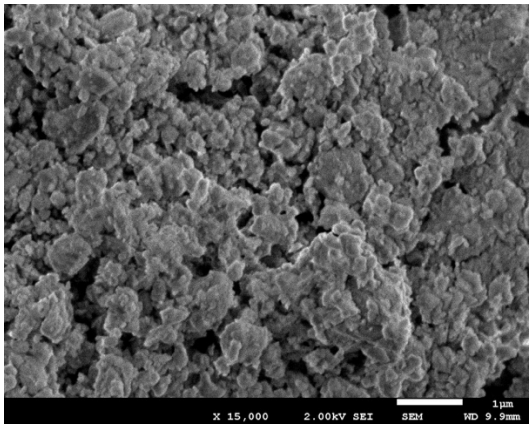

Figure 34 : Magnesium milled 4 hours with 4 mL of methanol – SEM x15000

These 3 pictures show clearly the morphology of the powder milled 4 hours, which is quite similar to the powder of Magnesium milled 2 hours.

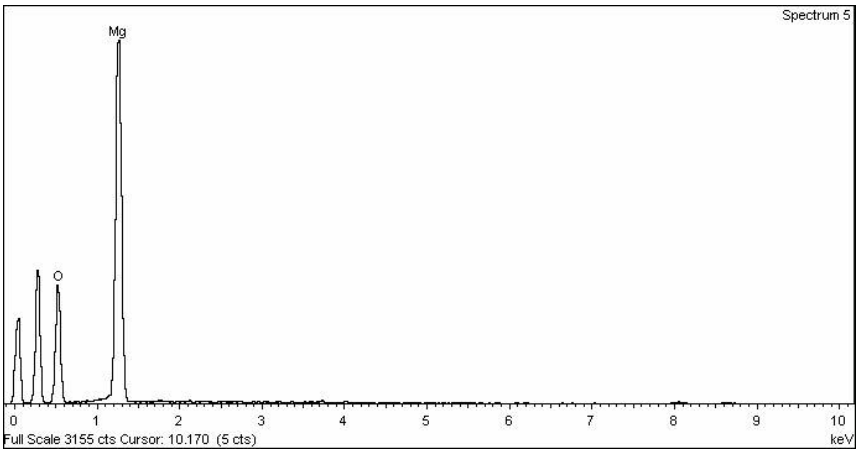

Figure 35 : Magnesium milled 4 hours with 4 mL of methanol – Spectrum

As for the previous powders, the spectrum looks like the same, there are still no contaminations by other metals as the stainless steel from the balls or the vials.

This is now necessary to see if the milling time have a real impact on the particle sizes distribution and then on the hydrogen absorption of the powder.

4.1.2. MgTi powder morphology

In order to try other composition, a mix of Magnesium and Titanium was done with 2/3 (weight) of Mg and 1/3 of a thin powder of Titanium.

The aim of this part is, as for the Magnesium powders, understand the morphology of this mix after different milling (1h, 2h and 4h).

Firstly, the samples that will be studied has been milled for 1 hour, with 4mL of methanol.

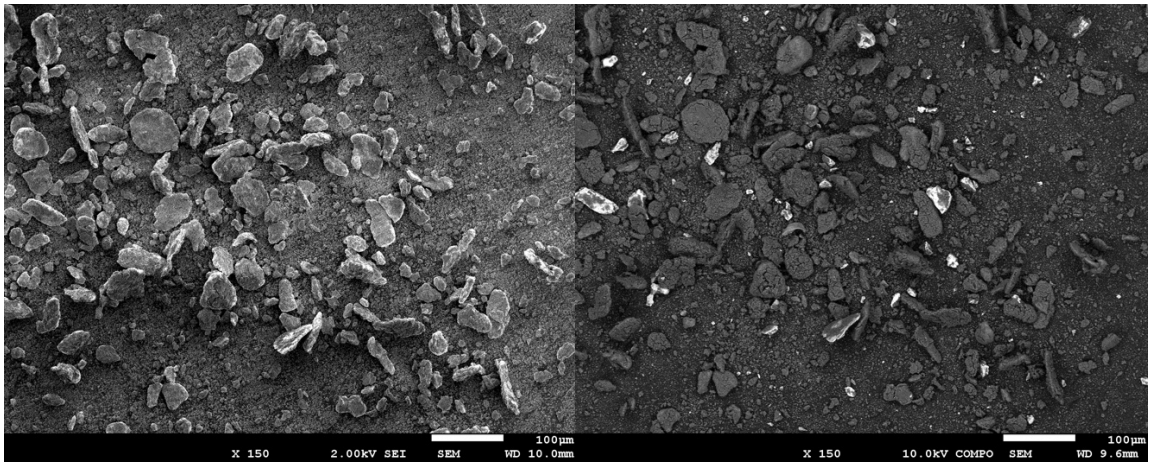

Figure 36 : MgTi milled 1 hour with 4 mL of methanol – SEM x150

These two pictures of magnification x150 will help to understand the morphology of the powders.

On the left one, it is observable that, as for the Magnesium, there are many small particles created by the mechanical milling. There are also still some bigger particles. The size distribution of the particles looks approximately like for the Magnesium powder at this magnification. Nevertheless, it is important to notice that the powder of Titanium used for the mix was thinner than the initial Magnesium powder, this could explain the presence of many small particles.

The picture of right has been taken with backscattered electron in order to make the composition more visible. The particles which look like silvered are the particles of Titanium. It is observable that there are more particles of Magnesium and that most of the particles of Titanium are smaller than the Magnesium ones.

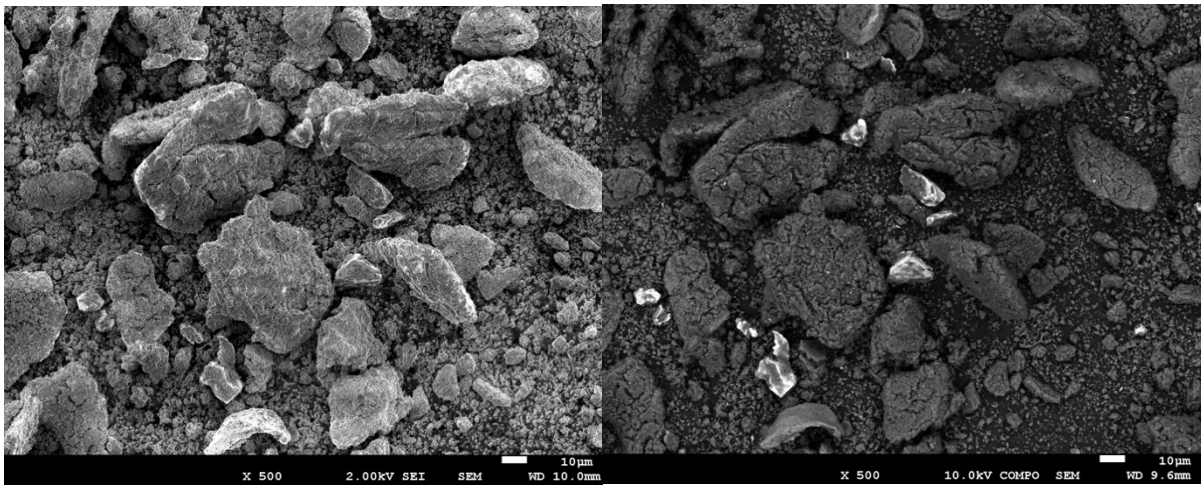

Figure 37 : MgTi milled 1 hour with 4 mL of methanol – SEM x500

On these two pictures, the size distribution also looks approximately as the Magnesium powder. Indeed, the milling is effective and reduced the size of the particle. On the right picture, it is also observable that the bigger particles have many cracks which could be created by the mechanical milling. It means the milling is efficient because the specific surface area is increased. However, it is important to notice that many parameters have to be taken in count.

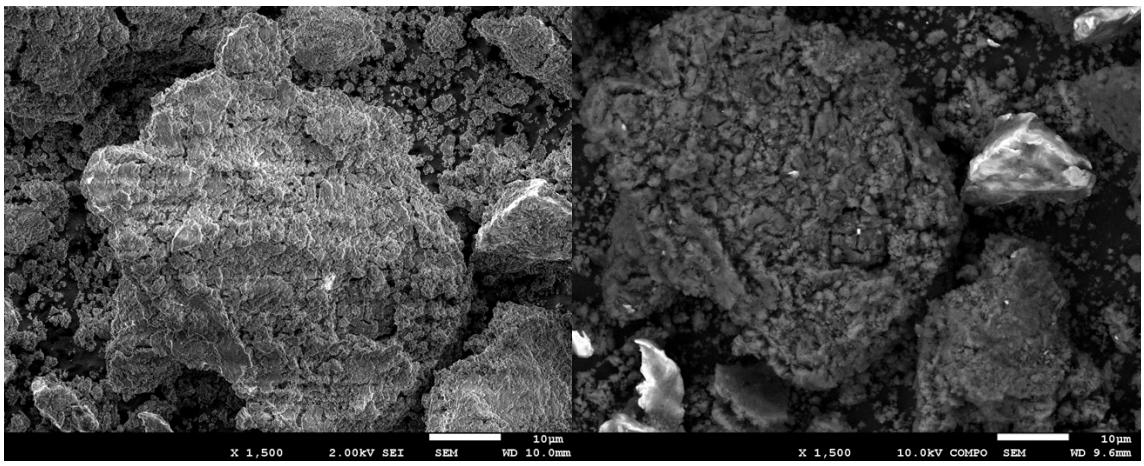

Figure 38 : MgTi milled 1 hour with 4 mL of methanol – SEM x1500

By using the magnification x1500, it is possible to see if the mix has been done properly. Indeed, thanks to the backscattered electrons, the composition is visible. Then, it is observable that the mix has been done properly in some places of the samples but not everywhere. Titanium and Magnesium haven't been mixed totally. In order to obtain a homogeneous mix, the particles should be smaller.

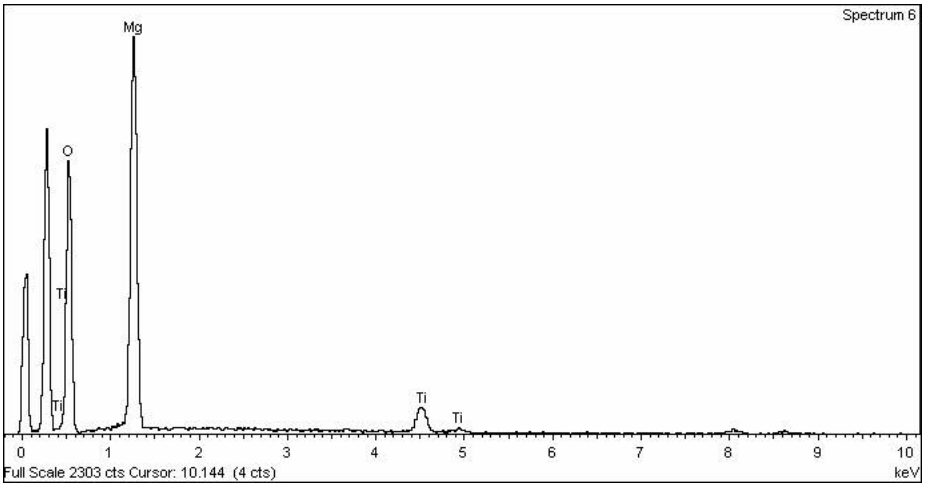

Figure 39 : MgTi milled 1 hour with 4 mL of methanol – Spectrum

Concerning the spectrum obtained, it seems that there are still not so much contamination. Indeed, the peaks observable are those from Magnesium and Titanium as planned.

Secondly, the powder studied is the same as the first one but milled 2 hours instead of 1 hour.

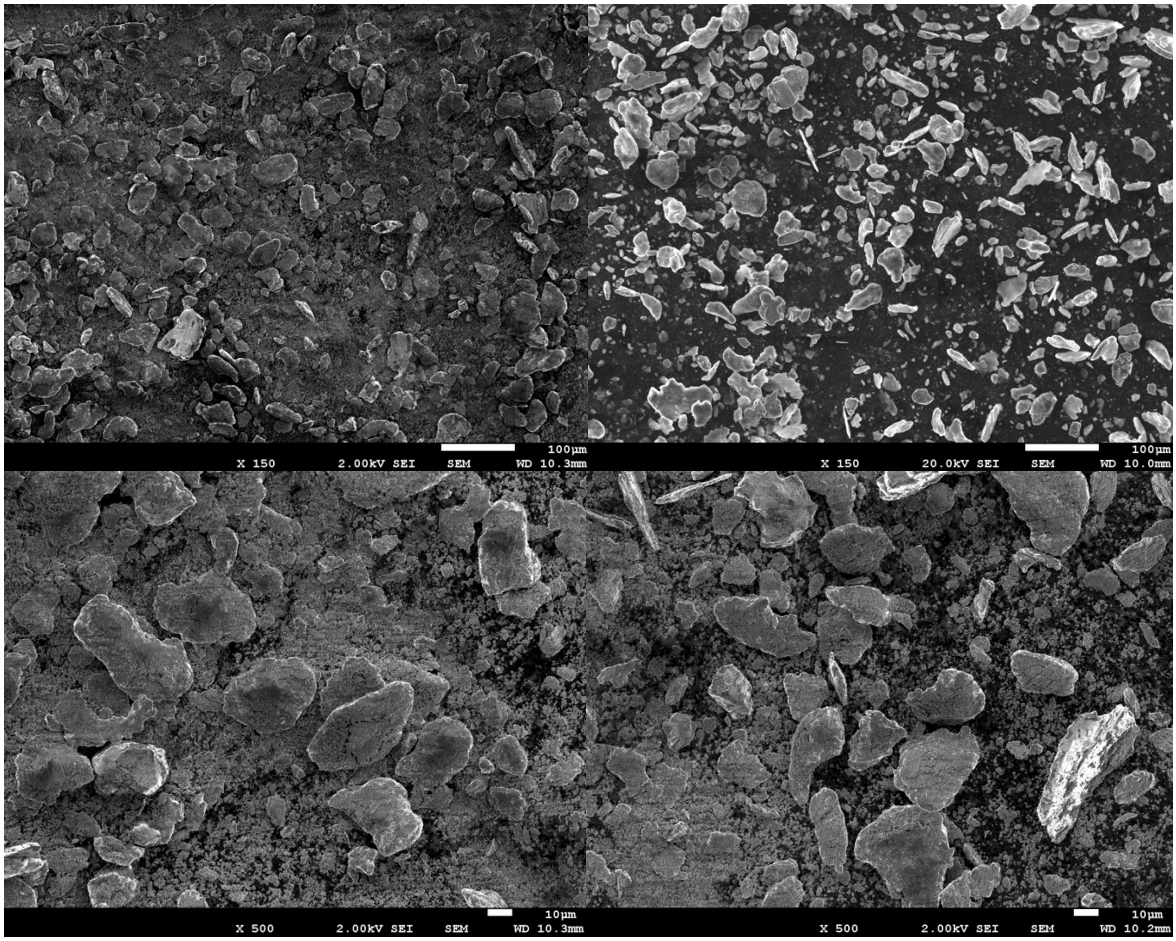

Figure 40 : MgTi milled 2 hours with 4 mL of methanol – SEM x150/500

These four pictures at low magnification show us the global morphology of the powder milled 2 hours. The morphology has no radical changes with this milling of 2 hours. It is also necessary to analyse the others characterisation tests as the PSD but the mix seems not to be totally done.

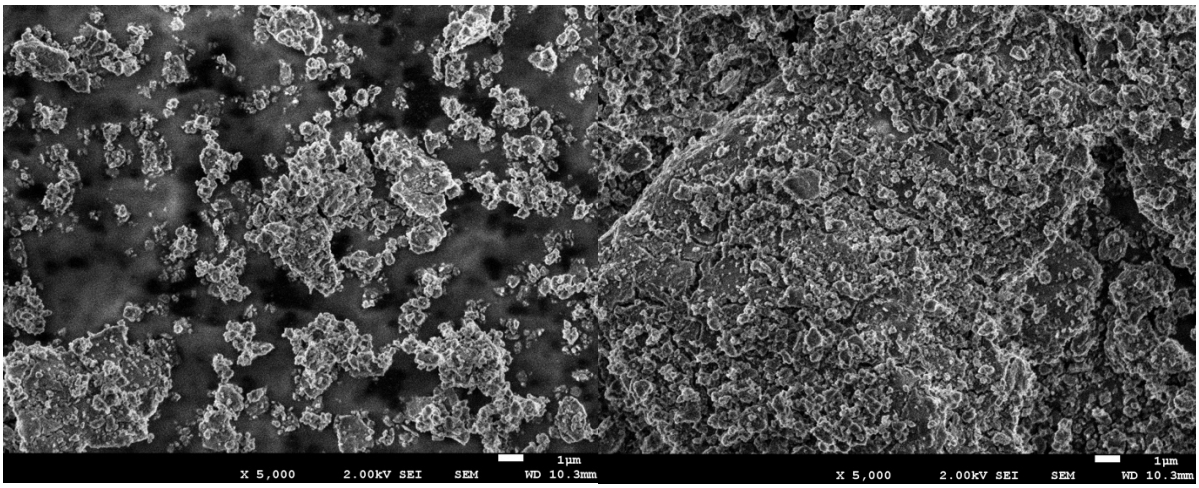

Figure 41: MgTi milled 2 hours with 4 mL of methanol – SEM x5000

Thanks to a higher magnification (x5000), it is now observable that some Titanium is well mixed into the Magnesium powder. However, the milling should be increased in order to get a better mix and create a uniform powder.

The third powder to study is the same in term of weight composition but this one was milled 4 hours.

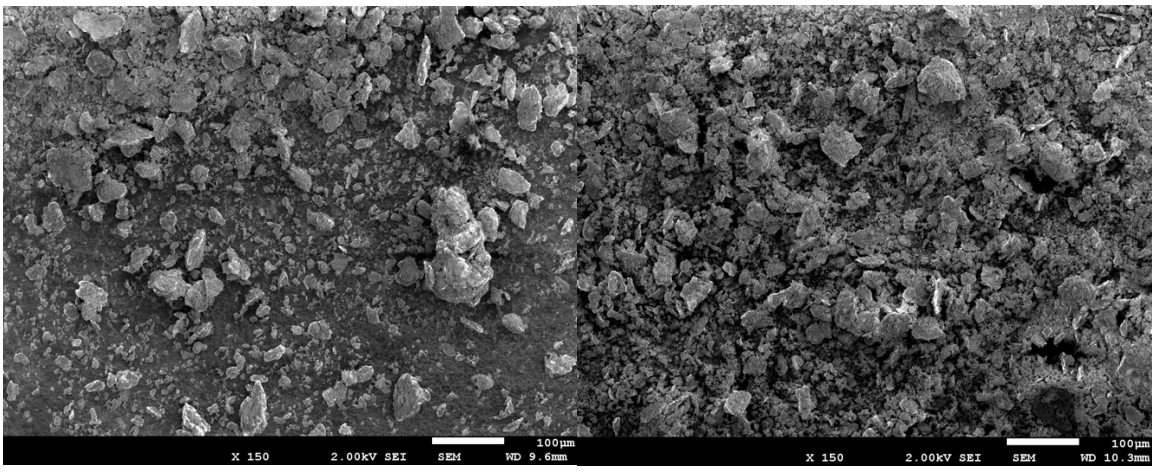

Figure 42: MgTi milled 4 hours with 4 mL of methanol – SEM x150

On these pictures, the size of the particles seems to be smaller thanks to the longer milling. The repartition of Magnesium and Titanium look more homogeneous.

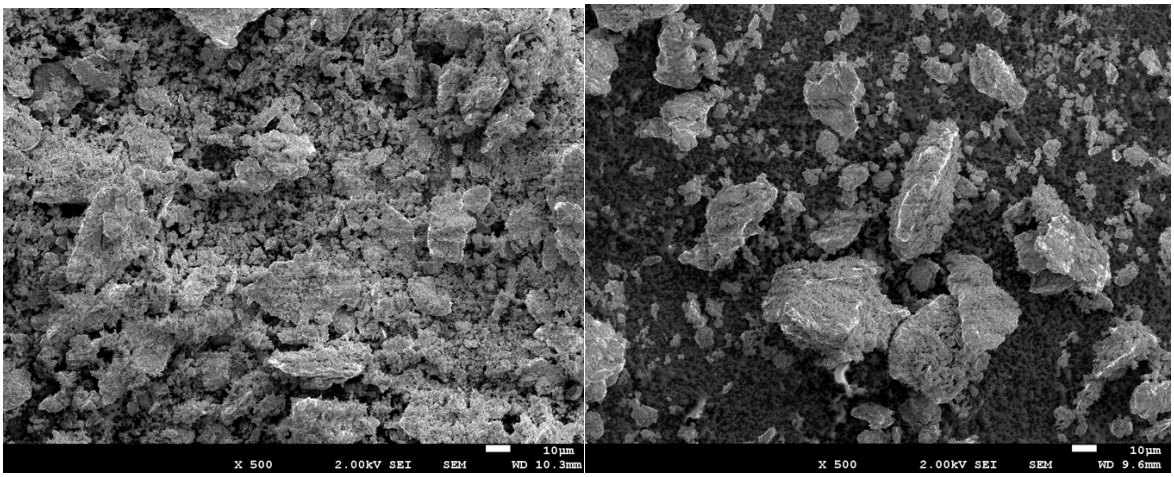

Figure 43: MgTi milled 4 hours with 4 mL of methanol – SEM x500

Even if there are some bigger particles which are not totally reduced into small particles, the milling looks efficient on these pictures.

In order, to see how the mix is done, it is possible to use a map.

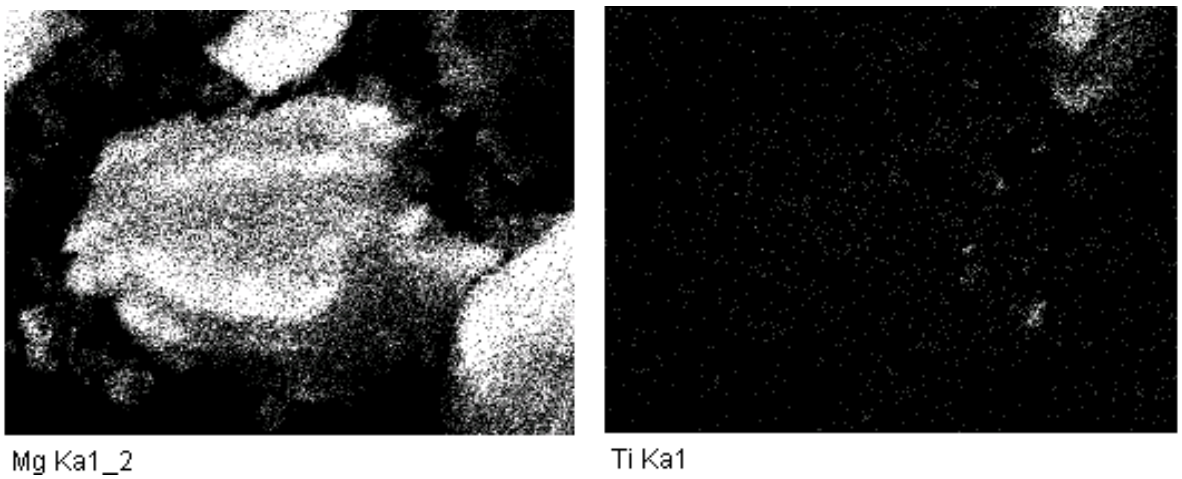

Figure 44: Map of Magnesium and Titanium

These pictures help to understand the morphology and the repartition of the particles. It is observable that even if it looks like it is better mixed with 4 hours milling, the mix is still not totally done.

4.1.3. MgTiFe powder morphology

The third powder studied is composed with Magnesium, Titanium but also Iron. The composition chosen was 4/6 (weight) of Magnesium, 1/6 of Titanium and 1/6 of Iron.

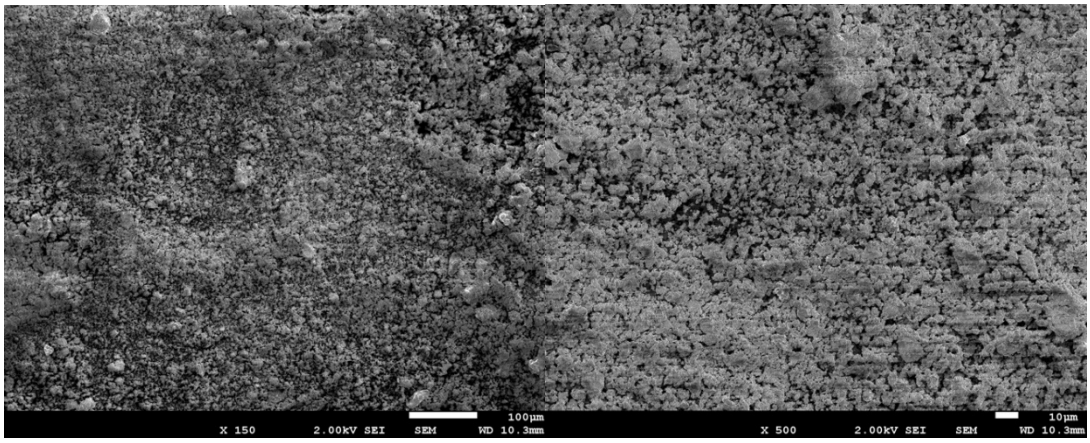

Figure 45: MgTiFe milled 1 hour with 4 mL of methanol – SEM x150/500

On these pictures with low magnification, it is observable that the particles seem to be smaller than for other mix. Indeed, it is hard to distinguish the different metal in this mix. It means that the milling with Methanol has a good effect on the particle's sizes.

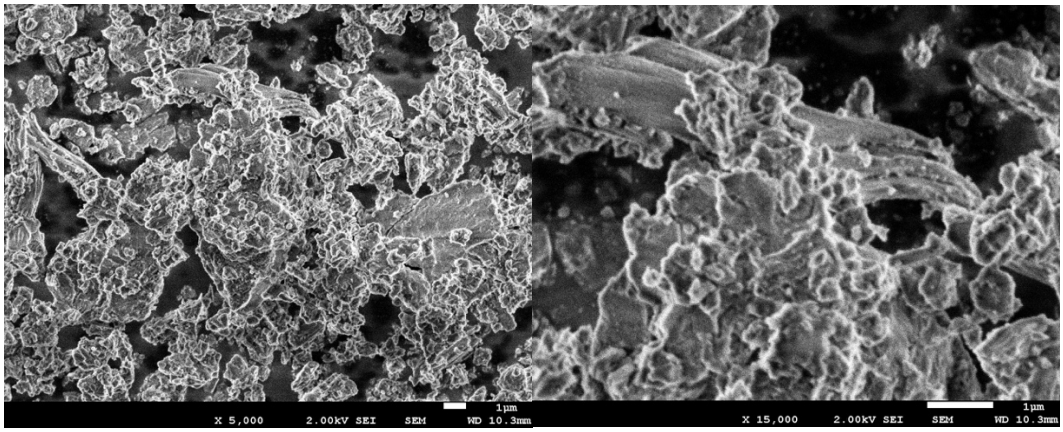

Figure 46: MgTiFe milled 1 hour with 4 mL of methanol – SEM x5000/15000

This is clearly visible that all the particles have been mechanically deformed by the milling. There are many angles which increase the specific surface area.

In order to see the repartition, the map will also be used for this sample.

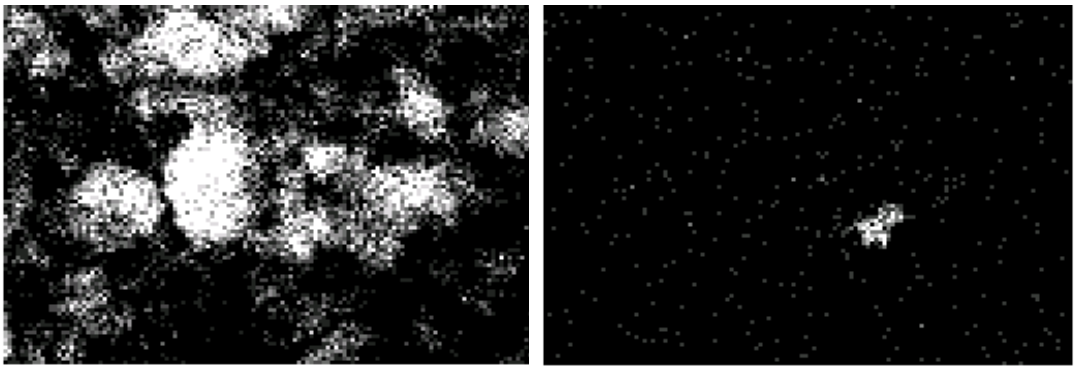

Figure 47: Map of Magnesium and Iron.

Thanks to the map, it is visible that the repartition doesn't seem to be better. Some solutions have to be found in order to obtain a better mix between the powders used.

4.2. Metal powder composition

In order to study the metal powder composition, it is necessary to use the X-ray diffraction as it is explained in the experimental procedures part.

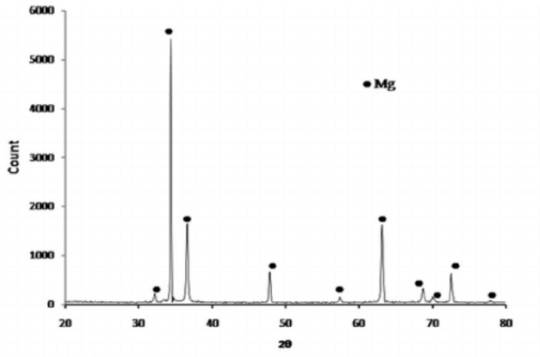

Figure 48: XRD Pattern of Magnesium[34]

Thanks to the pattern of Magnesium XRD, it is possible to compare the XRD obtained in our experiments.

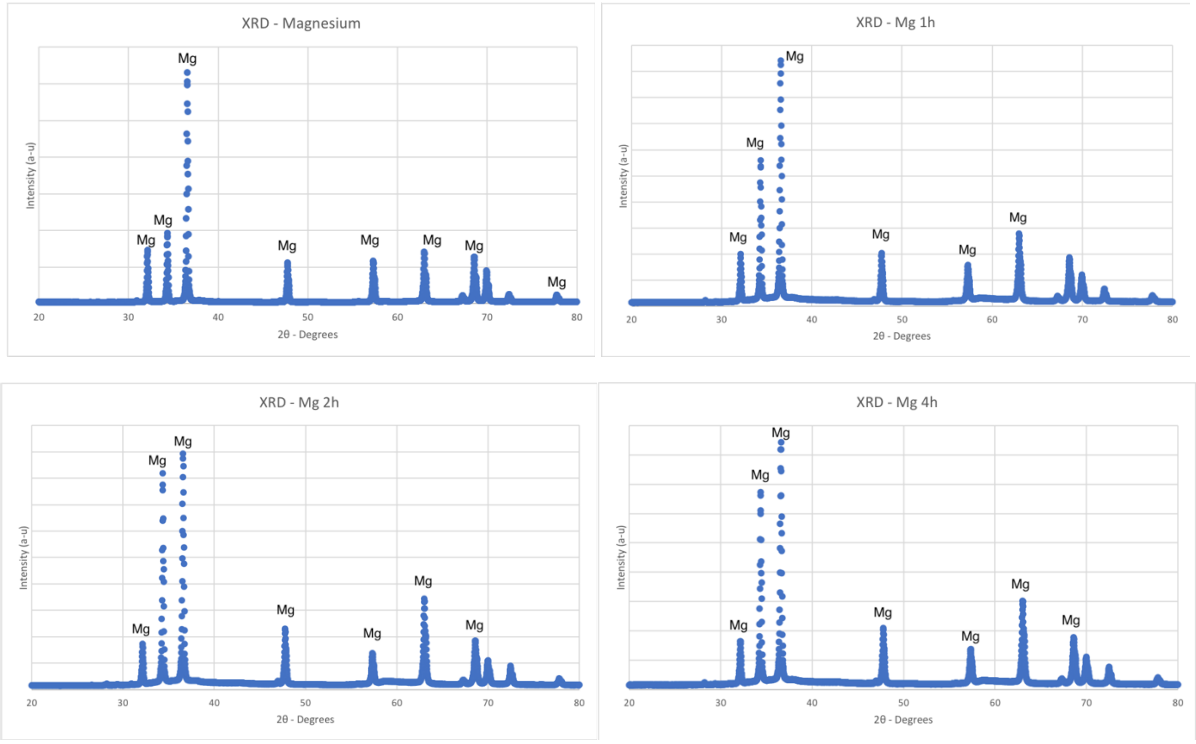

Figure 49: XRD Spectrum of 4 powders of Magnesium

Thanks to these graphs, it is visible that compared to the pattern of Magnesium, it is very similar. There are no high peaks except the one for Magnesium. It means the powder has not been contaminated or too much oxidized which will allow us to obtain better performances for hydrogen absorption.

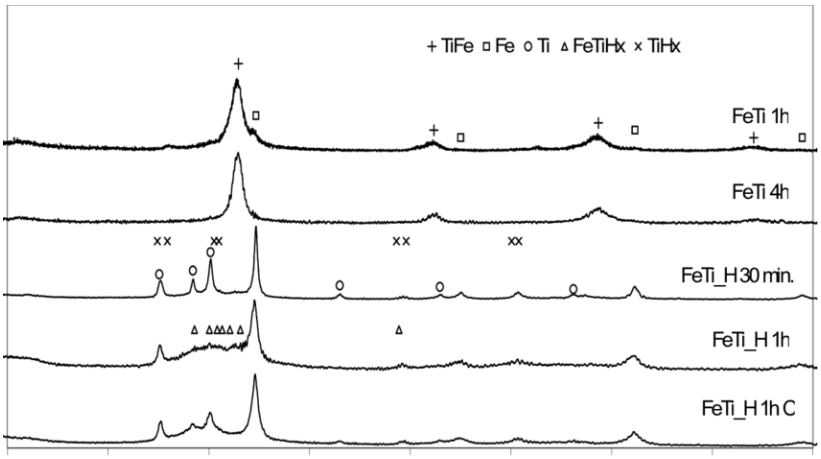

Figure 50: XRD Pattern of Fe and Ti[20]

On this pattern, there are most of the representative's peaks corresponding to FeTi, Fe and Ti which could be obtain by an X-ray diffraction. Then, it allows us to compare the XRD spectrum we obtained to this one.

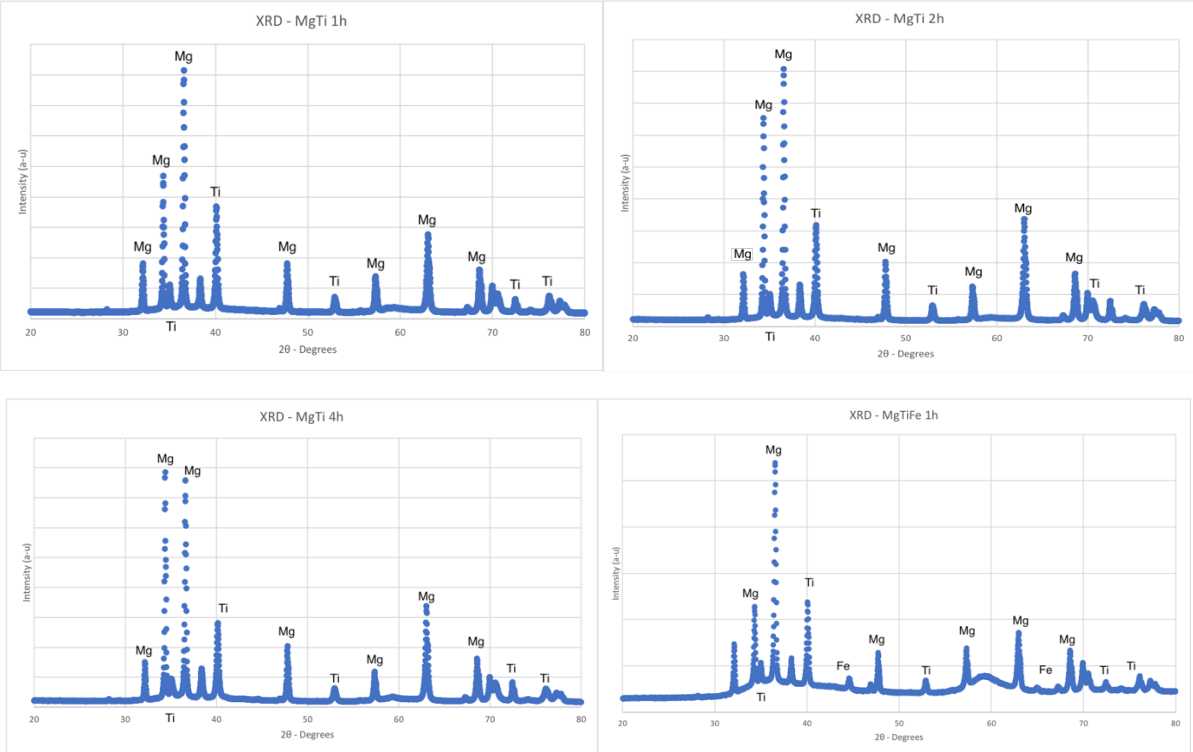

Figure 51 : XRD Spectrum of 4 others powders

These XRD spectrum allow us to see that there are still Magnesium peaks in each spectrum. However, it is also observable that there are many different peaks corresponding to Titanium (and Iron in the last one). Nevertheless, there are no peaks corresponding to intermetallic as FeTi. It means that the mix still has to be improved with a milling with better conditions. There is no solid solution where Fe, Mg and Ti are solved. Indeed, a solution could be found by increasing the energy or the time for the milling.

4.3. Particle size distribution

In this part, the particle size distribution will be studied. For each sample, 3 measures were made and then the average was done in order to obtain better results.

4.3.1. Magnesium powder PSD

4.3.1.1. Magnesium

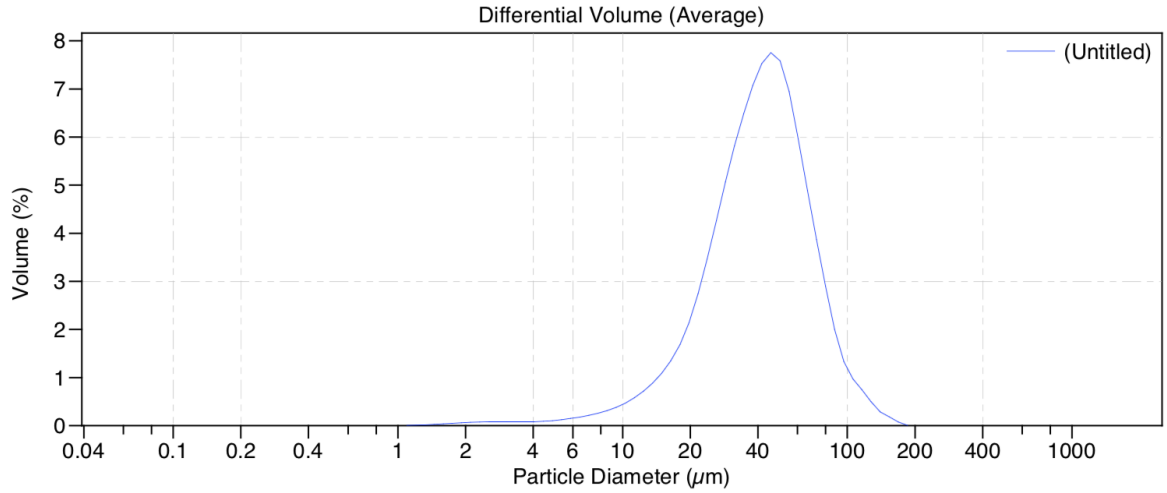

Figure 52: PSD for Magnesium

As it is observable on the graph, the particle diameter of the initial Magnesium is between 2 micrometres and 200 micrometres. Nevertheless, the biggest amount of the particles (in volume) is between 20 and 100 micrometres.

4.3.1.2. Magnesium milled 1 hour

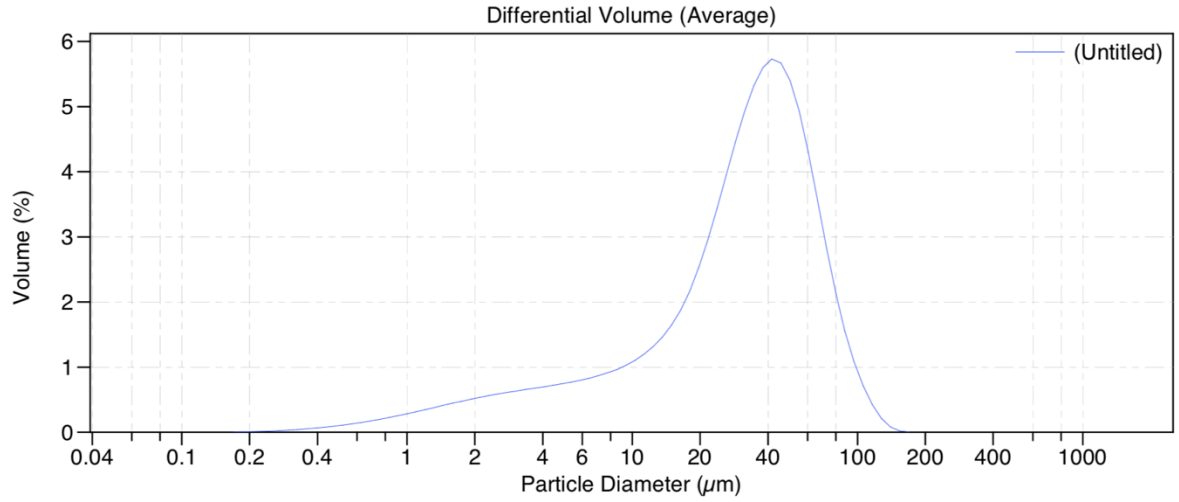

Figure 53: PSD for Magnesium milled 1 hour

When this graph is compared to the first one, it is visible that the repartition of the size of the particles has changed. Indeed, there are still a big volume of large particles, but it is less (only 6%). Moreover, the slope is different on the graph, there are more particles with a smaller diameter (between 1 and 10 micrometres).

4.3.1.3. Magnesium milled 2 hours

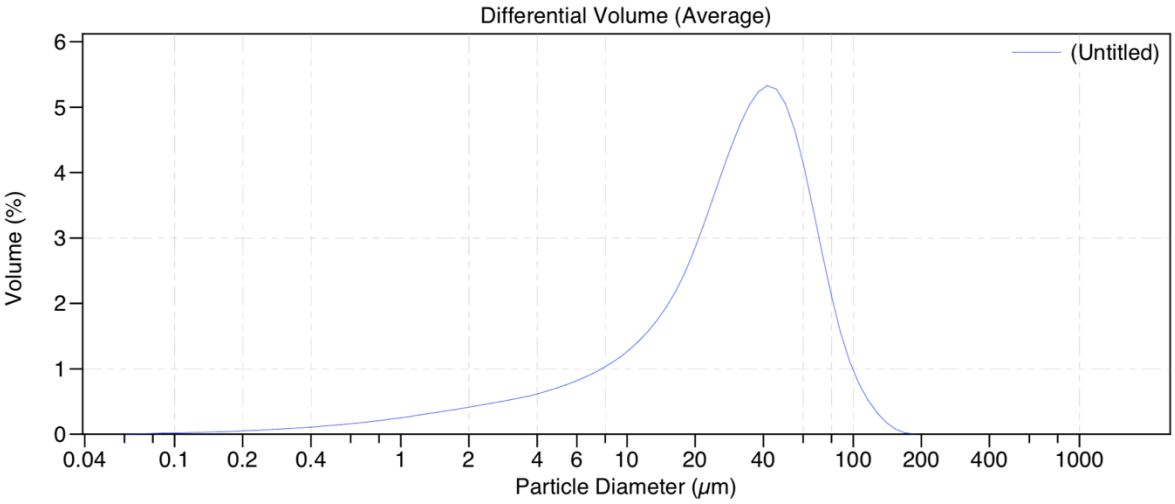

Figure 54: PSD for Magnesium milled 2 hours

The repartition seems to be almost the same as for the Magnesium milled 1 hour. However, there is a difference, indeed there are approximately of 1% in volume of particles with diameter between 6 and 8 micrometres while it was 1% in volume between 8 and 10 micrometres for the previous powder.

4.3.1.4. Magnesium milled 4 hours

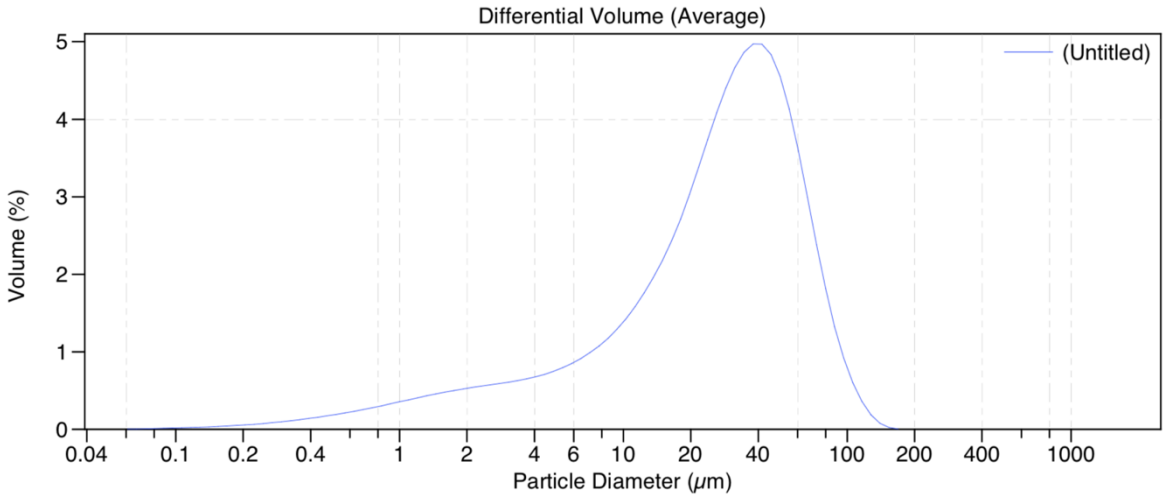

Figure 55: PSD for Magnesium milled 4 hours

As for the previous powder, the change is not so radical. However, the volume of smaller particles still increases and show us clearly that the milling is efficient even if the change is not very important. However there are many agglomerates created as it is visible on the graph for the volume of bigger particles.

4.3.2. MgTi powder PSD

4.3.2.1. MgTi milled 1 hour

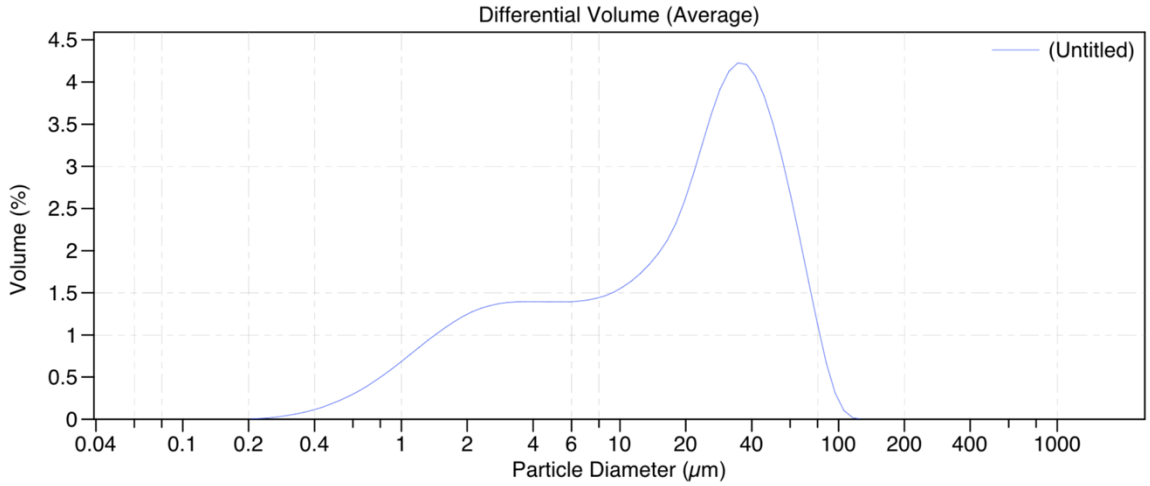

Figure 56: PSD for MgTi milled 1 hour

The graph is totally different compared to the Magnesium powder. This is due to the fact that the powder of Titanium used is originally thinner than the Magnesium one. Then there are more particles with a diameter between 0,4 and 10 micrometres.

4.3.2.2. MgTi milled 2 hours

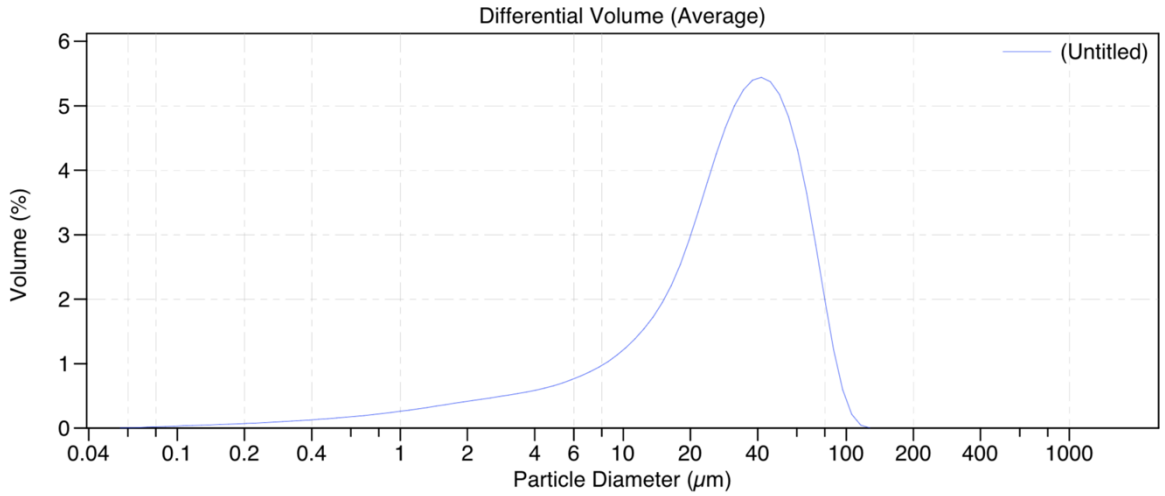

Figure 57: PSD for MgTi milled 2 hours

The graph shows us that the volume of small particles has decreased. However, there are some particles which are smaller than for the first sample of MgTi, then it seems like the milling has been efficient.

4.3.2.3. MgTi milled 4 hours

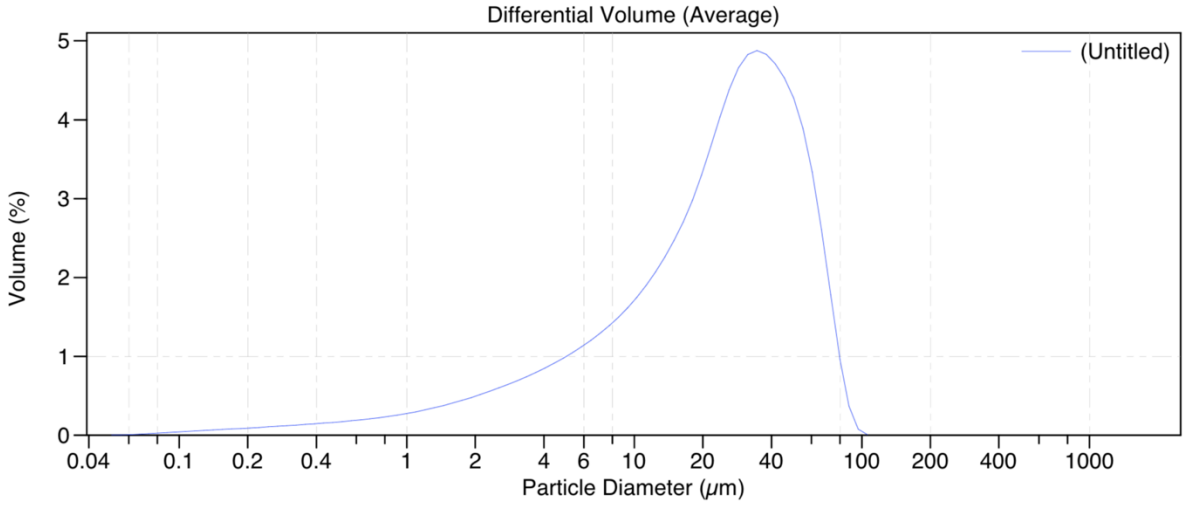

Figure 58: PSD for MgTi milled 4 hours

As seen previously, the volume of smaller particles has increased, and the volume of the bigger particles has a bit decreased.

4.3.3. MgTiFe powder PSD

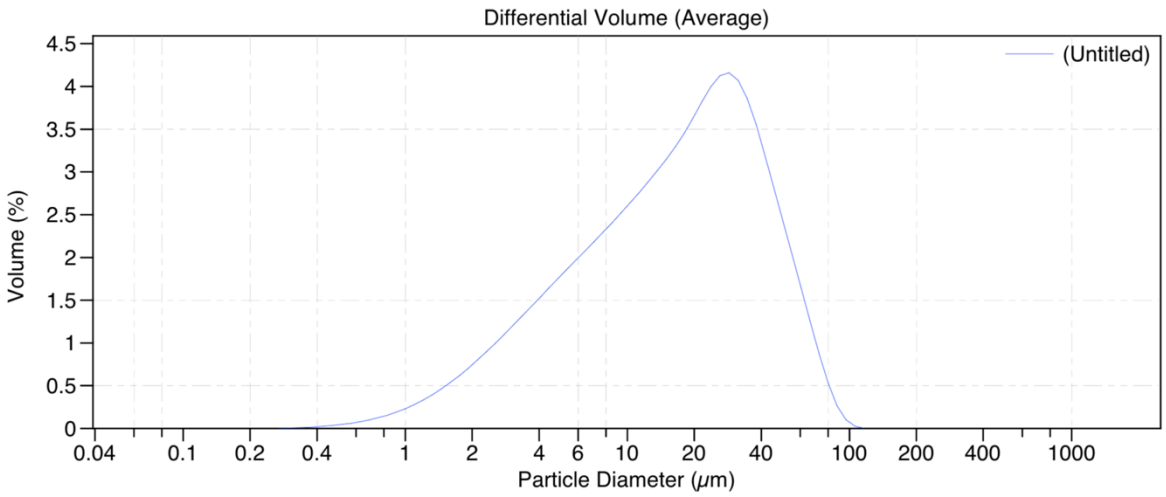

Figure 59: PSD for MgTiFe milled 1 hour

The graph for this mix of powders show us clearly that the volume of smaller particles is larger than for the other powders with a milling of 1 hour. Furthermore, the slope is regular while it wasn't for the other powders. It is important to notice that for this mix of powders, the Titanium powder used was thicker than for the MgTi powders.

4.4. BET analysis

4.4.1. Magnesium powder BET

In this part, the report from the BET test will be studied in order to know more about the specific surface area which is a really important parameters to improve the hydrogen absorption.

Powder	Surface area
Magnesium	0.8626 m2/g
Magnesium milled 1 hour	75.7176 m2/g
Magnesium milled 2 hours	71.2037 m2/g
Magnesium milled 4 hours	67.8603 m2/g

Figure 60: Table of the surface area for Magnesium powders

These results clearly show the difference between the not milled and the milled Magnesium powder, indeed, the surface area went from 0.8626 to 75.7176 m2/g with only an hour milling. This help us to understand that the milling is a great way to improve the surface area of a powder and then improve its capacity to absorb hydrogen.

However, there are almost no difference between the powder milled 1 hour and 2 hours. The light difference of surface area could be due to the agglomerates created during the milling of 2 hours which will decrease the surface area.
As seen previously, the results for the 4 hours milling decrease a bit too, probably due to the same problem. However, the surface area doesn't change that much but is still a lot larger than the original powder of Magnesium not milled.

4.4.2. MgTi powder BET

Powder	Surface area
MgTi milled 1 hour	79,0604 m2/g
MgTi milled 2 hours	75,1550 m2/g
MgTi milled 4 hours	62.2016 m2/g

Figure 61: Table of the surface area for MgTi powders

The surface area of the powder is a bit higher than the Mg powder milled 1 hour, this could be due to the fact that the Titanium powder used for the mix is thinner.
But, as for the Magnesium powders, the surface area seems to decrease with the increase of the milling time, but these changes are small.
However, by increasing the milling time to 4 hours, the surface area seems to decrease a lot. Indeed, the result has almost decreased of 15%. Probably due to the agglomerates which make the surface area decrease.

4.4.3. MgTiFe powder BET

Powder	Surface area
MgTiFe milled 1 hour	205,3341 m2/g

Figure 62: Table of the surface area for MgTiFe powders

As it is visible on the results, the surface area is the highest of all the samples. Indeed, it is more than the double of the best result for the other powders. In order to understand why this surface area is so high, it is interesting to study the SEM characterisation of this powder. Indeed, it was visible that there are many angles on the particles of this powders. Furthermore, the powder seemed to be very thin. These arguments could explain why the surface area has so much increased.

4.5. Hydrogen absorption test

4.5.1. Hydrogen absorption calculation

In order to calculate the hydrogen absorption with the data collected, it is necessary to use the equation: $PV = ZnRT$

To use this, all the data will be known, except the Z which has to be calculated thanks to the thermodynamic tables of the literature.

Then it is necessary to calculate the n, which is the moles of Hydrogen. Finally, considering M=2 g/mol. This is now easy to calculate the mass of hydrogen. Thanks to the mass of hydrogen, the percentage of absorption is calculated and then plot in function of the time (and so the temperature).

In order to calculate the Z factor, which is the compression factor, a linear regression is used on Excel.

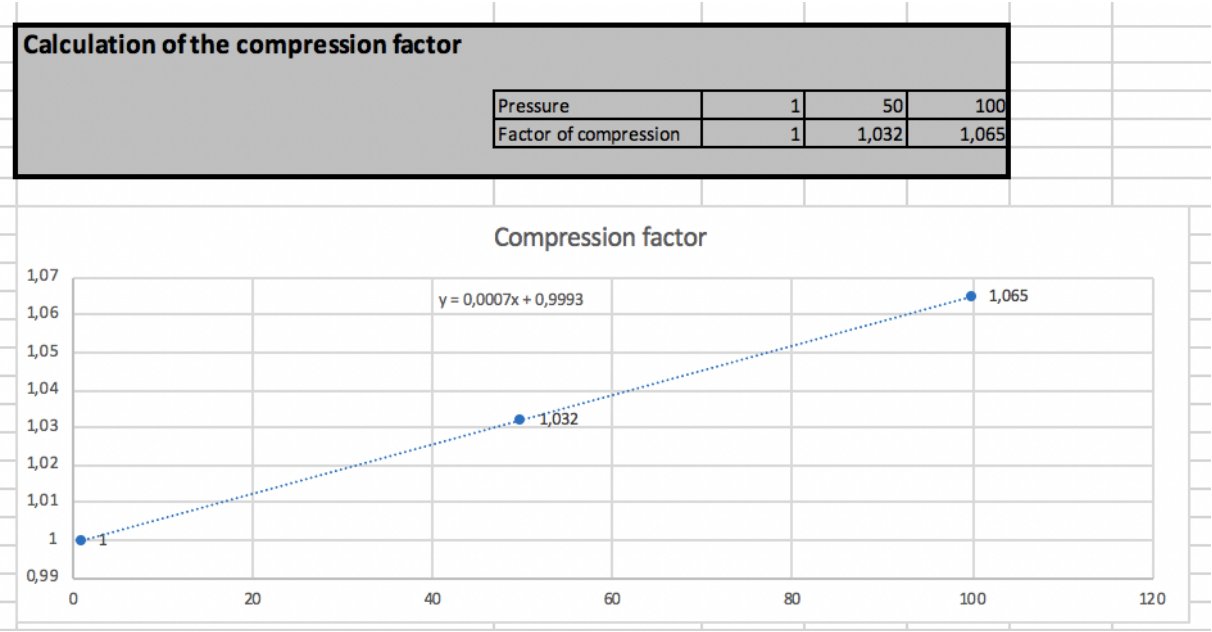

Figure 63 : Linear regression used to find the factor of compression

4.5.2. Hydrogen absorption measurements

For each powder, the hydrogen absorption has been tested. The powders were tested thanks to the system created in the Procomame laboratory. Thanks to the thermocouple and the Arduino card, data were collected. Finally, reported on a table, three list of data were obtained: Time, temperature and pressure. Then, calculations were made in order to plot the different graphs.

4.5.2.1. Magnesium powders

4.5.2.1.1 Magnesium milled 1 hour

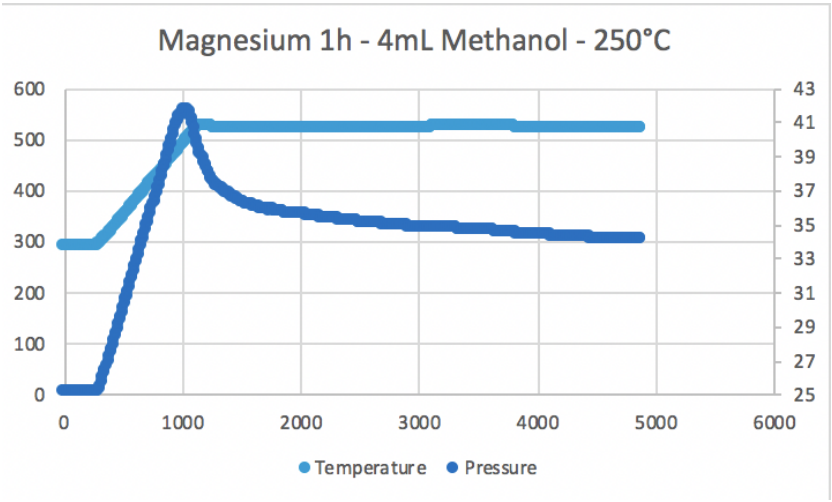

Figure 64: Temperature and pressure VS Time for Mg milled 1 hour

For this powder, it is observable that there is a decrease of pressure when the final temperature is reached. After reaching the temperature needed, it was stabilized for an hour and then cooled down. It is important to notice that the volume used is constant.

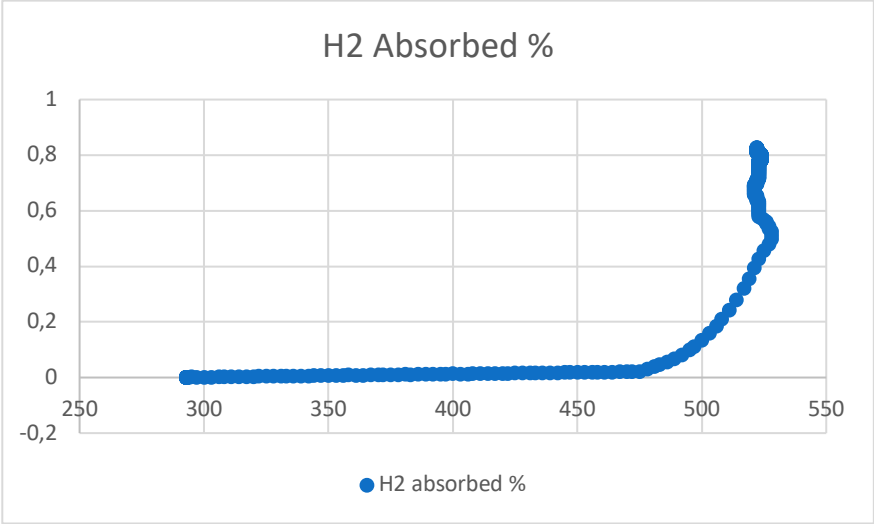

Figure 65: %H_2 absorbed VS temperature

After calculation on the table software, it is visible that as planned before, the absorption starts at 475°K approximately. The absorption increases quickly after reaching the temperature point. Finally, the absorption percentage obtained is 0,825 % (according to the calculation) which is quite a good result considering this powder was only milled 1 hour.

4.5.2.1.2 Magnesium milled 2 hours

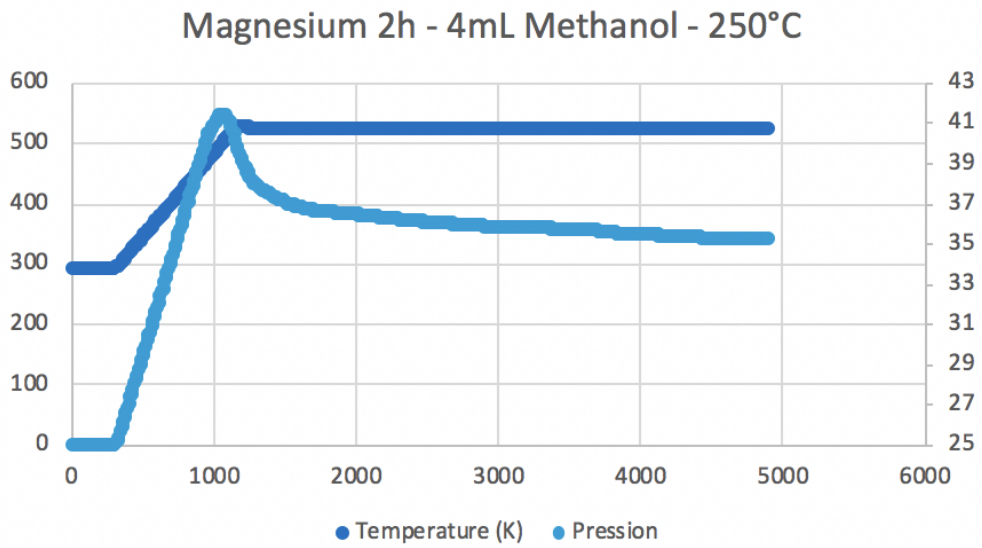

Figure 66: Temperature and pressure VS Time for Mg milled 2 hours

As for the previous sample, the absorption seems to begin at 1000s approximately. Then, the pressure also decreases due to the hydrogen absorption. In order to see the absorption differences between those two samples. It is necessary to study the absorption percentage graph.

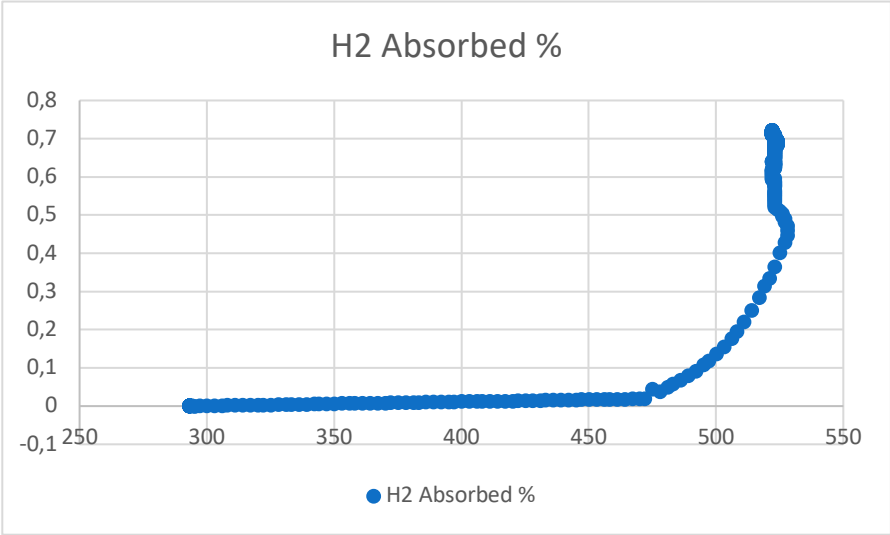

Figure 67: %H_2 absorbed VS temperature

Comparing this sample to the first one, it is visible that the absorption is not as efficient as in the first case. Indeed, the percentage of hydrogen doesn't reach 0,8%. Thanks to the calculation, we know that the percentage was: 0,721%.

This could be related to the PSD study where it was visible that with 2 hours milling, the surface area decreased a bit.

4.5.2.1.3 Magnesium milled 4 hours

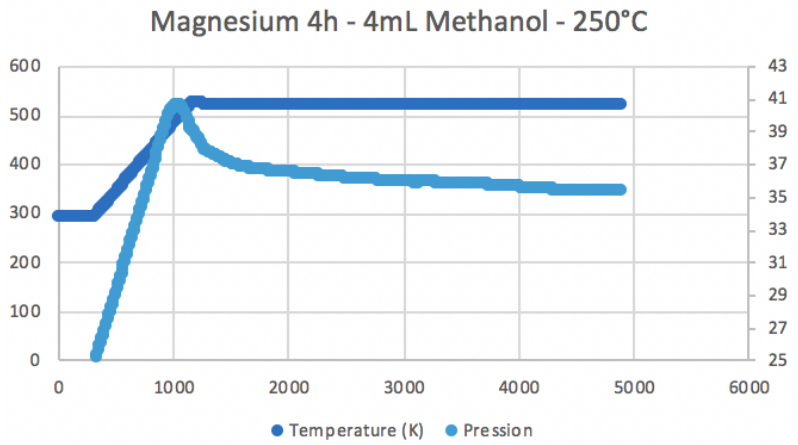

Figure 68: Temperature and pressure VS Time for Mg milled 4 hours

As for the previous powders of Magnesium powders, the absorption stars at the same moment. Nevertheless, the final absorption can still change.

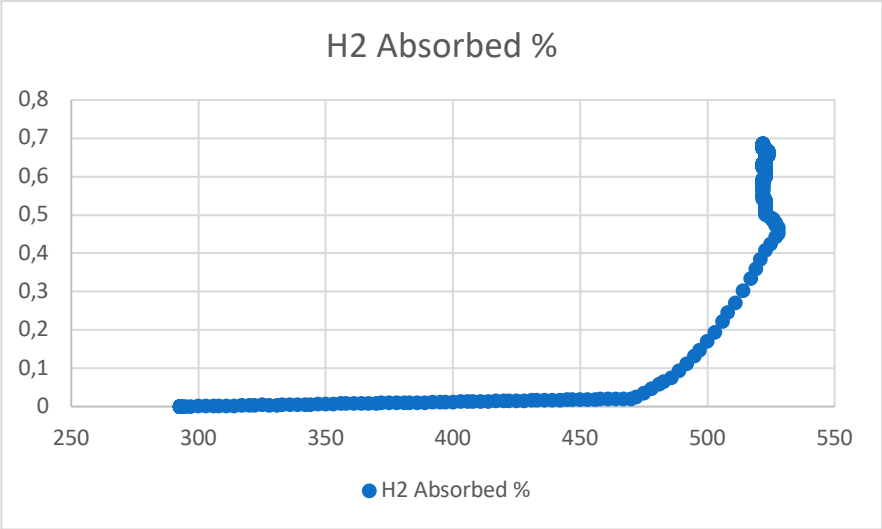

Figure 69: %H_2 absorbed VS temperature

Thanks to this graph, the fact that the increase of the milling time not obviously increase the hydrogen absorption is pointed. Indeed, the surface area didn't change that much, it even decreased. Furthermore, the oxidation and the contamination could increase while the specific surface area and the size of particles don't change a lot. Then, the oxidation would create a layer which avoid the hydrogen absorption.

Indeed, for this sample, the final absorption was: 0,686%

4.5.2.2. MgTi powders

4.5.2.2.1 MgTi milled 1 hour

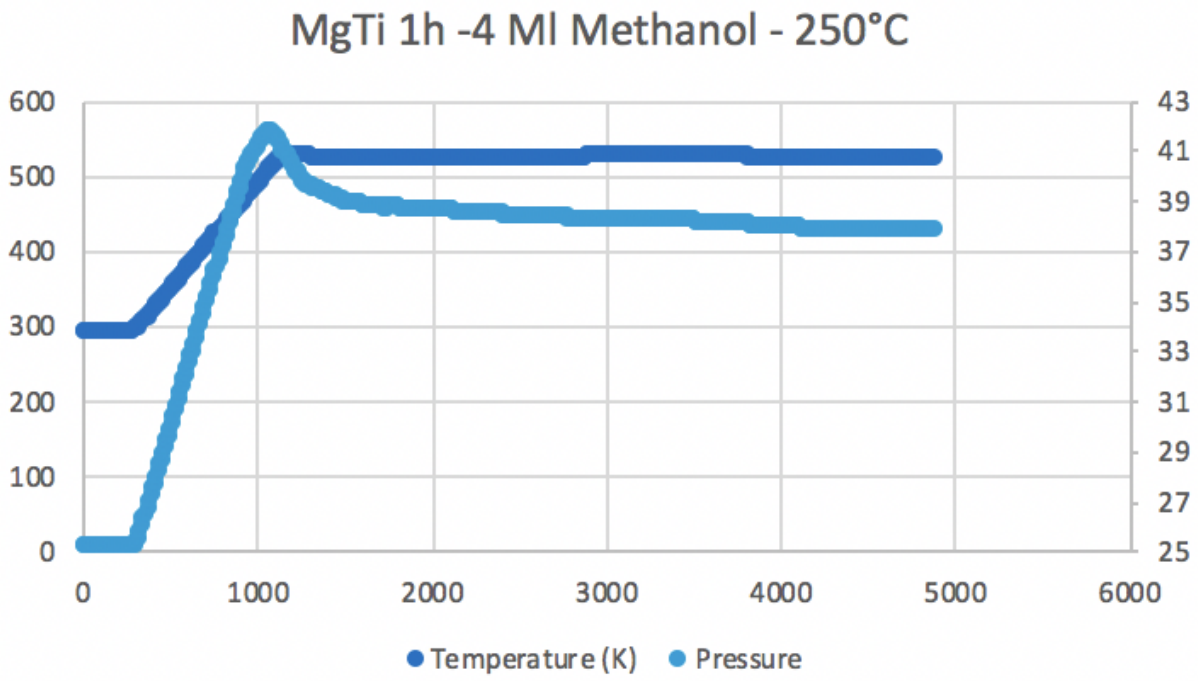

Figure 70: Temperature and pressure VS Time for MgTi milled 1 hour

For this sample, it seems like the fact of adding Titanium powder didn't change that much the range of temperature where absorption start. Indeed, the range is still the same. Nevertheless, the range could change by using a mix of Magnesium and Titanium better mixed. As it was visible with the SEM images, the mix is not done perfectly, then it could be improved.

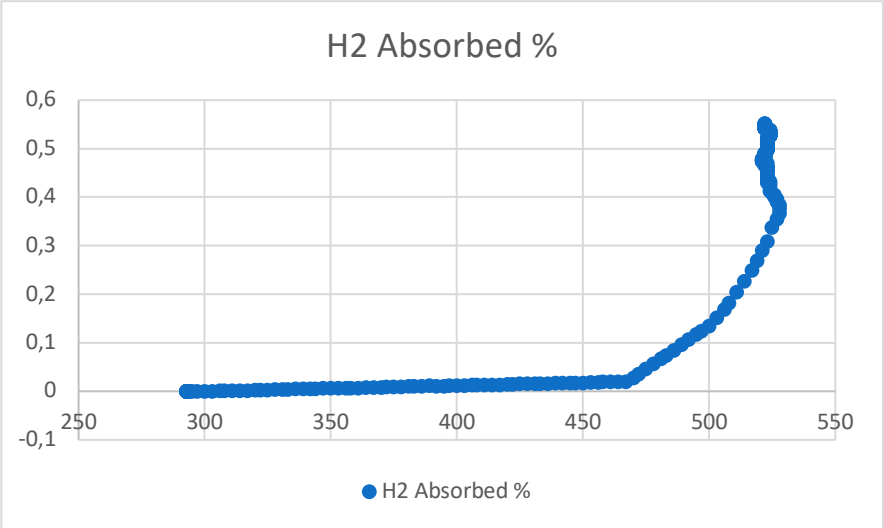

Figure 71: %H_2 absorbed VS temperature

Finally, doing the calculation and plotting the absorption percentage in function of time, it is clearly visible that the absorption is less important than for the powder of Magnesium. The absorption only reaches: 0,551%.

4.5.2.2.2 MgTi powder milled 2 hours

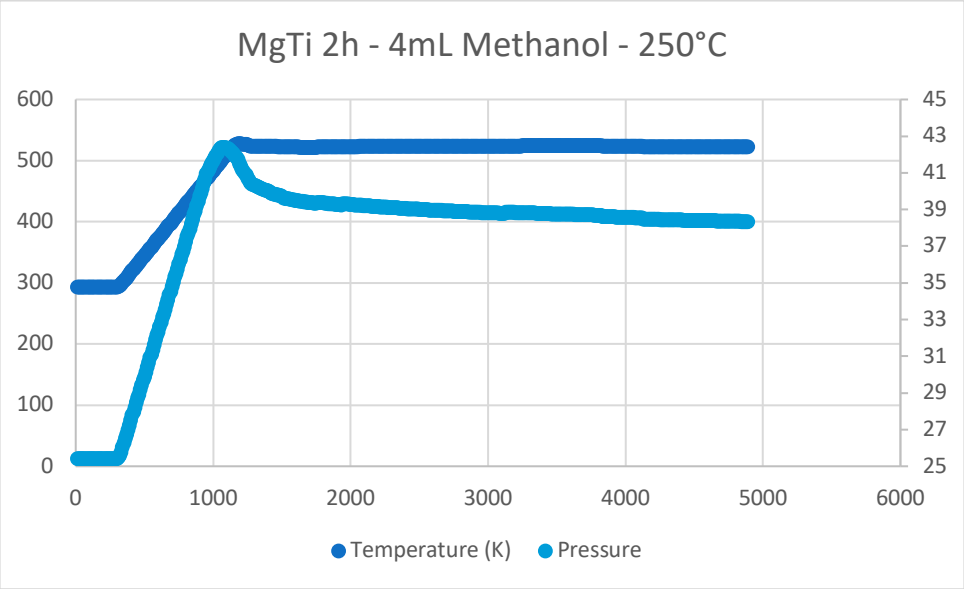

Figure 72: Temperature and pressure VS Time for MgTi milled 2 hours

The range of pressure and temperature where the absorption starts are still the same. Then it is visible that the time of milling doesn't affect that much the range of absorption. The fact is that a good mix between the metal could help to get a better hydrogen absorption range.

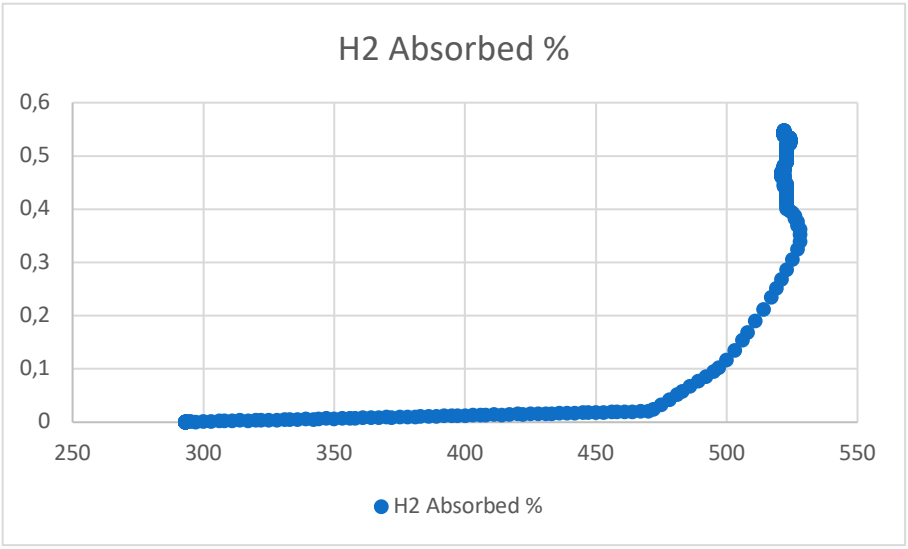

Figure 73 : %H_2 absorbed VS temperature

The final absorption calculated for this sample is about: 0,547%.

Considering some approximations in the calculation, the hydrogen absorption is the same for MgTi 1 hour milled and 2 hours milled is the same. As it was on the SEM pictures, no radical changes in the mix were visible. Furthermore, the fact that hydrogen absorption is lower could be explained by the size of the particles. Indeed, the size decreases while the specific surface area increases. Then, as for the Magnesium powders, the oxidation could increase and avoid absorption.

4.5.2.2.3 MgTi powder milled 4 hours

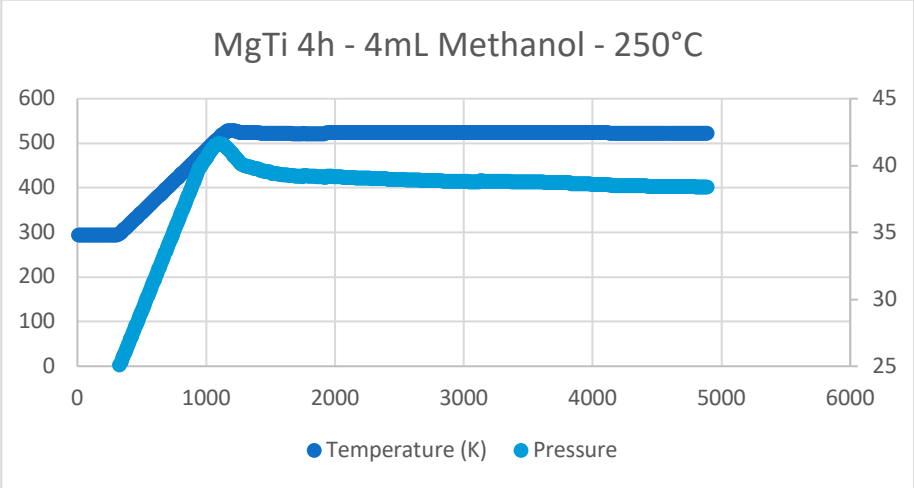

Figure 74: Temperature and pressure VS Time for MgTi milled 4 hours

About this sample, it is visible that the pressure decreases less than for other samples, but it is due to the fact that the absorption wasn't very important. Concerning the range of start of absorption, it doesn't change.

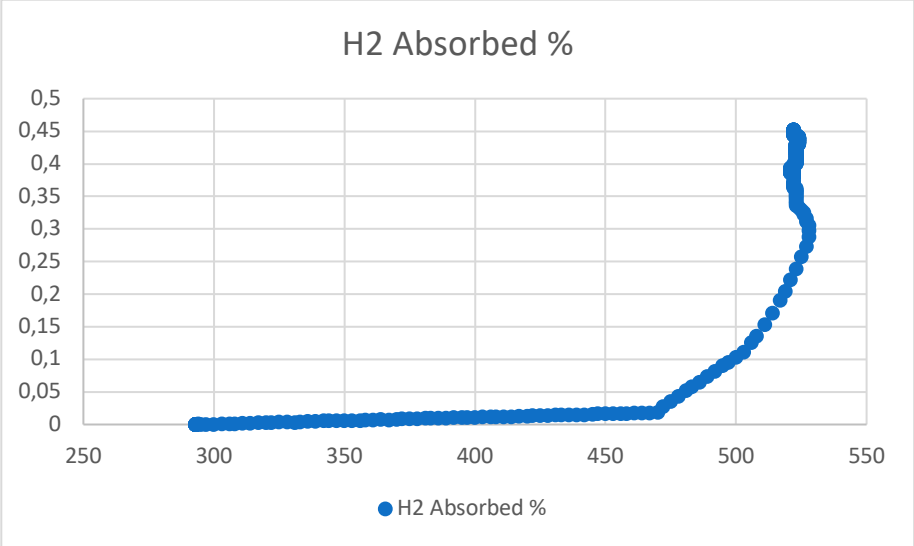

Figure 75: %H_2 absorbed VS temperature

The final absorption obtained after calculation was: 0,452% which is almost the half of the absorption obtained with the Magnesium milled 1 hour.

Then for the mix of Magnesium and Titanium, it is important to find some new parameters to change for the milling in order to get better properties of hydrogen absorption.

4.5.2.3. MgTiFe powder

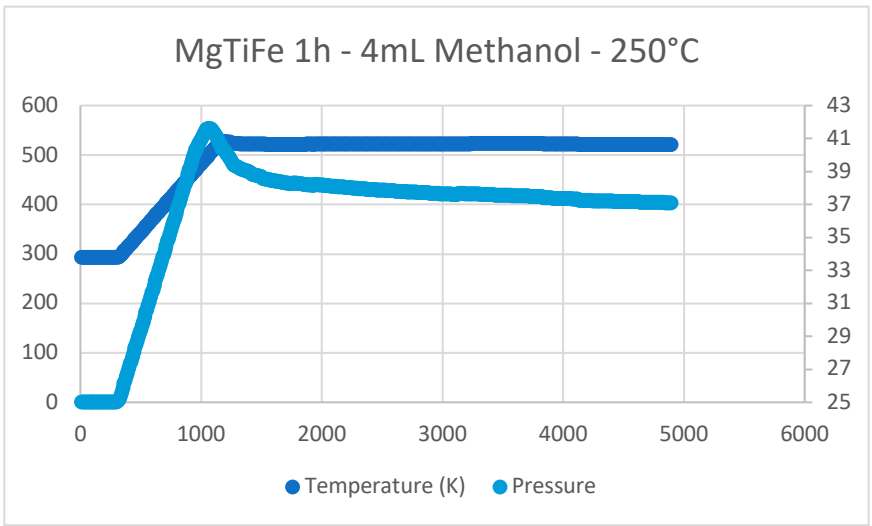

Figure 76: Temperature and pressure VS Time for MgTiFe milled 1 hour

By adding the powder of Iron in the mix, it helps to get a better absorption compared as the MgTi powder. Indeed, as it was visible with the PSD test, the surface area is very important,

and it could increase a lot the absorption. However, it is important to avoid the contamination and the oxidation to get better hydrogen absorption properties.

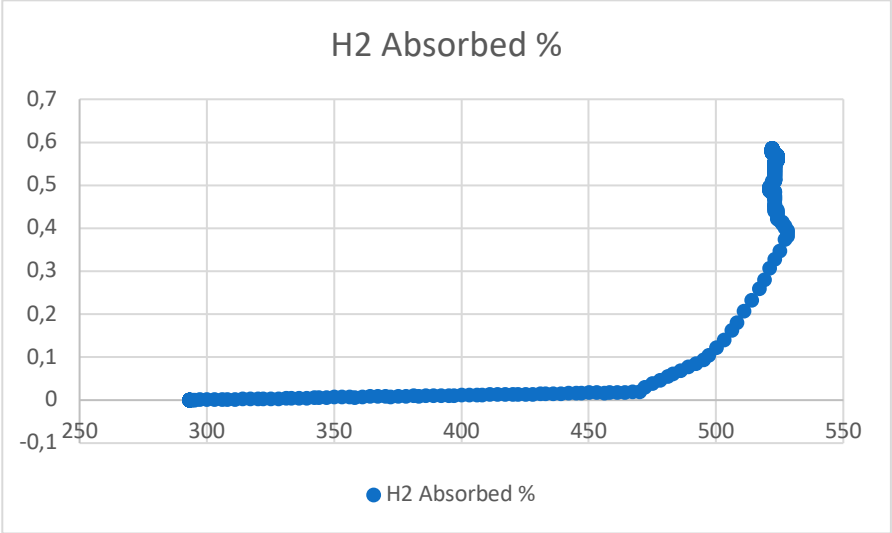

Figure 77: %H_2 absorbed VS temperature

Considering the fact that the sample was only milled 1 hour, the absorption results are quite good. Nevertheless, it would be probably necessary to mill this powder more in order to get a higher surface area and a better mix between the metals in the sample.

The final absorption for this sample is then: 0,585% which is still higher than the MgTi powders.

4.5.3. Absorption results

Powder tested	Absorption percentage
Mg milled 1 hour	0,825 %
Mg milled 2 hours	0,721%
Mg milled 4 hours	0,686%
MgTi milled 1 hour	0,551%
MgTi milled 2 hours	0,547%
MgTi milled 4 hours	0,452%
MgTiFe milled 1 hour	0,585%

By studying this table with all the results, it is visible that the increase of the milling time doesn't increase the absorption percentage. The first hour of milling to activate the powder is necessary but the hours of milling after the first one don't help to increase the absorption, probably due to the creation of agglomerates.

Concerning the temperature where the absorption begins, for all the different powders, the temperature doesn't change. In order to improve this one, it could be possible to find new intermetallic or new milling parameters.

Moreover, the Magnesium powder seems to be the more interesting powder in order to get high hydrogen absorption. However, assuming that the powders of MgTi and MgTiFe were not totally mixed, it could be one of the problems which make the hydrogen absorption decreases.

CONCLUSION

Thanks to this project, many conclusions have been obtained.
First, it shows that it is necessary to activate the metallic powders by using mechanical milling. Indeed, without this, there are less surface area to absorb a high quantity of hydrogen. Furthermore, it important to find the good parameters for the milling, in order to have a good mix between the different metals that could be used. It is also important not to have too much agglomerates, that is why the choice of the control agent and its quantity (Methanol in our case) is crucial. Thanks to the results obtained, it is visible that the first hour of milling is very efficient because the specific surface area increases a lot. The particles of Magnesium break rapidly under a not very energetic parameters of milling. After an hour, the specific surface area decreases which means that there is no need to increase the milling time. Obviously, the aim is to reduce as more as possible the milling time, then a balance has to be found between all the parameters used for the milling.

Moreover, the different characterization tests show that, in order to obtain some intermetallic, it is also necessary to increase the milling time, speed or apply another treatment to the powder. Indeed, the mixing of Mg and Ti didn't result in the creation of intermetallic. Same results have been found with Fe. Then it is necessary to apply a more energetic milling in order to obtain intermetallic. Also, this could improve the hydrogen absorption capacity by reducing the oxidation and the contamination.

In brief, metallics powders are able to absorb hydrogen but the powder composition doesn't seem to affect a lot the hydrogen absorption. The percentage of hydrogen absorbed has to be improved in order to use this method industrially, but this could be an alternative for the storage of hydrogen in the future. Indeed, increasing the volume could be a solution in order to obtain more hydrogen absorption. Furthermore, the solid-state hydrogen storage is the best method of storage in terms of volume used. In order to continue this project, it could be interesting to try different milling parameters in order to obtain a large surface area with some intermetallic powders.

As a conclusion, solid state hydrogen storage seems to be a solution in the future. Some points as the percentage of absorption and the range of temperatures has to be improved in order to obtain an economic way of storage in addition to an eco-friendly and gasless energy source.

Economic analysis and Budget

In this part, the economic aspect of the project will be tackled, in order to present the spending necessary to work on this topic.

Considering the fact that the powders are counted in the final price of the project.

Name	Price	Quantity
Planetary ball mill	5€/load	16
Hydrogen bottle 3HH (150 bars 3L) – Extra pure	55€	1
Material and machining	400€	-
X-ray diffraction	250€	-
SEM Analysis	300€	-
Arduino/Picolog software	0€	-
Particle size distribution	15€	7
BET	120€	7
Lab Manager	60€/h	15
Project director	60€/h	30
Mechanic	45€/h	25
Salary	12€/h	720
Total		14245€

Table 1: Economic analysis

The total spending for this project is then 14245€.

Environmental impact analysis

The aim of this chapter is to analyse the impact of the experiments led during this project concerning the environment.
The amount of metal used for all the experiment is little. Indeed, only 6 grams of metal was used for each milling. In total, 16 milling were done, then only 96 grams of metal were used. Then, no contamination could occur. Furthermore, all the manipulations were done under protective atmosphere which reduce again the possible risks. Moreover, a mask was carried in order not to breathe thin particles of metal powders.

Even if hydrogen is explosive and magnesium can flame, the whole system used was dimensioned in order to get a safe environment. Indeed, the tank and the container were able to carry a pressure of 225 bars while the work was carried at 20 bars approximately. In case of the Magnesium combusts, some silica sand was kept in hand in order to extinguish metallic fires. Finally, considering the low amount of hydrogen used, even in case of explosion, there would be no danger for the human life or the environment.

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